Dye catalyzed oxidation of refractory organic wastes using visible light energy
by Jerome Wadsworth Sargent

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Civil Engineering
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Abstract:
Dye sensitized aerobic photo-oxidation is a photo-chemical process by which some organics refractory to conventional waste treatment can be oxidized. Sensitizer dye absorbs visible light energy and transfers it to dissolved oxygen to form singlet oxygen. Singlet oxygen is a strong oxidizing agent capable of oxidizing various refractory organics including heterocyclic aromatics like cresol and phenol. The oxidation products are likely to be nonaromatic compounds tractable to biological oxidation. With sunlight as the light source only oxygen and energy for aeration are consumed.

The sensitizer can be reused many times if a method of dye applica tion and recovery is developed. Some dyes might serve as sensitizers while irreversibly bound to polymers like ion exchange resins, polysaccharides, or polymeric gels. After substrate photo-oxidation, polymer and dye could be removed by sedimentation, screening, or some other method.

Methylene blue and Rose Bengal are effective sensitizers of aerobic photo-oxidation of phenol and cresol. Minimum cresol half-life is 2.45 minutes with methylene blue and 2.74 minutes with Rose Bengal. Phenol half-life is 6.9 minutes with methylene blue and 7.5 minutes with Rose Bengal.

High pH (9 to 10) favors dye sensitized aerobic photo-oxidation. Reaction rate increases with increasing light intensity from tungsten incandescent lamps. Light from commercially available fluorescent lamps is not sufficiently intense to energize the process. Substrate oxidation can be achieved in liquid layers up to 1 3/4 inches thick.

Optimum methylene blue concentration to sensitize aerobic photooxidation of cresol and phenol is 1.56 10-5M. Optimum initial substrate concentration is about 4.5 x 10-4M.

Attaching methylene blue to various commercially available cation exchange resins significantly reduces the dye's ability to sensitize singlet oxygen production. Further testing is necessary to develop a method by which dye can be applied and recovered for reuse without detracting from its ability to absorb visible light and generate singlet oxygen.

For the technologic and economic feasibility of dye sensitized aerobic photo-oxidation applied to waste treatment to be assessed, the process must be tested with sunlight and actual waste streams.

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ABSTRACT

Dye sensitized aerobic photo-oxidation is a photo-chemical process by which some organics refractory to conventional waste treatment can be oxidized. Sensitizer dye absorbs visible light energy and transfers it to dissolved oxygen to form singlet oxygen. Singlet oxygen is a strong oxidizing agent capable of oxidizing various refractory organics, including heterocyclic aromatics like cresol and phenol. The oxidation products are likely to be nonaromatic compounds tractable to biological oxidation. With sunlight as the light source only oxygen and energy for aeration are consumed.

The sensitizer can be reused many times if a method of dye application and recovery is developed. Some dyes might serve as sensitizers while irreversibly bound to polymers like ion exchange resins, polysaccharides, or polymeric gels. After substrate photo-oxidation, polymer and dye could be removed by sedimentation, screening, or some other method.

Methylene blue and Rose Bengal are effective sensitizers of aerobic photo-oxidation of phenol and cresol. Minimum cresol half-life is 2.45 minutes with methylene blue and 2.74 minutes with Rose Bengal. Phenol half-life is 6.9 minutes with methylene blue and 7.5 minutes with Rose Bengal.

High pH (9 to 10) favors dye sensitized aerobic photo-oxidation. Reaction rate increases with increasing light intensity from tungsten incandescent lamps. Light from commercially available fluorescent lamps is not sufficiently intense to energize the process. Substrate oxidation can be achieved in liquid layers up to 1 3/4 inches thick.

Optimum methylene blue concentration to sensitize aerobic photo-oxidation of cresol and phenol is 1.56×10^{-5} M. Optimum initial substrate concentration is about 4.5×10^{-4} M.

Attaching methylene blue to various commercially available cation exchange resins significantly reduces the dye's ability to sensitize singlet oxygen production. Further testing is necessary to develop a method by which dye can be applied and recovered for reuse without detracting from its ability to absorb visible light and generate singlet oxygen.

For the technologic and economic feasibility of dye sensitized aerobic photo-oxidation applied to waste treatment to be assessed, the process must be tested with sunlight and actual waste streams.

CHAPTER I

INTRODUCTION

Photo-oxidation is the oxidation of a substrate by means of a series of chemical reactions involving light energy. The various different kinds of photo-oxidation processes are legion so it is necessary to describe carefully and completely a particular photo-oxidation sequence being discussed. The process which is the subject of this report, dye sensitized aerobic photo-oxidation, is described in an earlier paper by Sargent (1971).

The literature is replete with reports of scientific research on photo-oxidation and its almost unlimited applications. Less numerous but still extensive are references concerning application of various photo-oxidation processes to water and wastewater treatment. Virtually all of the latter deal with destruction of waste molecules or micro-organisms either directly or indirectly by ultraviolet light. Examples are the investigation by Bulla and Edgerley (1968) of photolysis of pesticides by ultraviolet light, the studies by Matsuura and Smith (1970) of UV energized photo-decomposition of formic acid and detergents, and testing of photochemical oxidation of soluble organics in municipal wastewater by Hancil and Smith (1971). Kinney and Ivanuski (1969) refer only incidentally to dye sensitized photolysis of waste materials.

Water or wastewater treatment processes which require ultraviolet light often prove uneconomical because of energy requirements. That disadvantage will only be aggravated as energy becomes an ever more scarce commodity. Dye sensitized aerobic photo-oxidation, however, is energized by visible light which suggests the possibility of using sunlight.

Most organic waste molecules are not destroyed by direct absorption of visible light. But, according to Kautsky (1938) and Foote (1968), many dyes like methylene blue and Rose Bengal will absorb visible light energy in water solution and selectively transfer that energy to dissolved oxygen. The oxygen is excited to a singlet state and becomes a strong oxidizing agent capable of oxidizing many ordinarily refractory organic molecules. After energy transfer to oxygen the dye is available to absorb more light energy. With sunlight as the energy source only oxygen and energy for aeration are spent.

Earlier studies by Sargent (1971) and Kolesnikov (1958), and unreported preliminary testing by Seely (1973) show that some organic materials which appear in some waste streams and are refractory to ordinary treatment processes can be destroyed by dye-sensitized aerobic photo-oxidation. Many investigators including Mathews (1963), Blum (1935), and Wallis et al (1972) have shown bacteria and viruses can be killed by the same method. But an engineering process to employ dye sensitized aerobic photo-oxidation in water or wastewater treatment has yet to be developed. One reason is that photo-chemistry is foreign to sanitary engineers and the gap between scientific research and engineering application has never been bridged.

For dye sensitized aerobic photo-oxidation to be successfully employed as a treatment process a means of applying, recovering, and reusing the sensitizer dye must be developed. Only a very low concentration of dye is required [1.5×10^{-5} molar (M)] but dyes are relatively expensive and consumptive use of dye should be avoided. One possible method of dye application and recovery is to bind the dye irreversibly to larger particles like ion exchange resins or polymeric gels. The dye can serve as a sensitizer while attached to the polymer and the polymer-dye complex can be removed for reuse by sedimentation, screening, or some other process. Several investigators have studied dye binding to polymers including Bellin and Yankus (1968), Bellin (1968), Vitagliano and Costantino (1969), and Bradley and Wolf (1959). With their work as guide, it is likely a dye sensitized aerobic photo-oxidation treatment process with little consumptive use of dye can be developed.

Dye might also be applied in solution to sensitize substrate oxidation followed by removal of the dye by ion exchange. But ion exchange resins are very selective for most dyes. Hence dye elution from the resin for reuse would probably be impractical, and both dye and resin could only be used once.

OBJECTIVES

The general purpose of this research is to analyze and optimize the important parameters of dye sensitized aerobic photo-oxidation as applied to water and wastewater treatment. Specific objectives are to:

1. Test fluorescent and tungsten incandescent lamps as energy sources for dye sensitized aerobic photo-oxidation.
2. Develop a reactor for testing dye sensitized aerobic photo-oxidation both in batch and flow-thru process as a water and wastewater treatment method.
3. Test several dyes for effectiveness as photo-sensitizers.
4. Determine the extent to which phenol and cresol can be photo-oxidized in a dye sensitized process using visible light.
5. Optimize substrate concentration, dye concentration, light intensity, and pH as parameters of dye sensitized aerobic photo-oxidation.
6. Determine the liquid layer thickness to achieve optimum photo-oxidation under the conditions of this investigation.
7. Compare reaction rates in batch and flow-thru processes.
8. Determine if dye attached to various different commercial ion exchange resins can sensitize aerobic photo-oxidation of substrate.

9. Test an ion exchange resin for capacity to remove sensitizer dye from aqueous solution.

LIMITATIONS

All experiments in this study were performed in the laboratory using a small reactor. No testing was done with sunlight or actual waste streams.

Of the great number of dyes with potential as sensitizers for aerobic photo-oxidation, nine were used in this study. Two substrates (phenol and cresol) representative of aromatic, heterocyclic waste materials were tested.

The reaction mechanisms involved in dye sensitized aerobic photo-oxidation are complex and not completely understood. Hence all parameters important to the process have not been defined. Several parameters of probable importance were studied in this investigation.

CHAPTER II

THEORY

GENERAL PHOTO-OXIDATION

Any chemical reaction or series of reactions which requires light energy and results in oxidation of some material can be called photo-oxidation. An almost unlimited number of different photo-oxidations are possible. One reason is many atoms and molecules can absorb light of proper wavelengths and be excited to energy states above their normal ground state. An atom or molecule thus excited or energized is a stronger oxidizing and reducing agent than its ground state. Hence absorption of light energy can cause oxidation which would not otherwise occur.

Greatly enlarging the number of possible photo-oxidation reactions is the fact that a given photo-chemical sequence can involve from one to several constituents as direct reactants, reaction intermediates, or catalysts. In fact a given set of primary reactants can react by many different pathways depending on such factors as temperature, pH, relative reactivity and concentration of reactants, and properties of the light source.

DYE SENSITIZED AEROBIC PHOTO-OXIDATION

REACTION SEQUENCE

Dye sensitized aerobic photo-oxidation is this writer's choice of a term to describe a particular photo-oxidation reaction, primary features of which are: (1) it is energized by visible light, (2) dye serves as the light absorber, (3) oxygen is required and consumed in a singlet state, and (4) a chosen substrate is irreversibly oxidized.

Energy Absorption

Most organic molecules which appear in wastewater streams are not destroyed by direct absorption of visible light. But dyes can be added which will absorb visible light to start a sequence of events resulting in oxidation of certain organics.

The ground state of dyes and most other molecules is a singlet. A singlet molecule is one which has all electron spins paired. Light absorption energizes the dye from ground state to an excited singlet state. An excited singlet still has paired electron spins but some electrons have been raised to higher energy orbitals. Excited singlet dye is very short-lived and either decays directly back to ground state singlet, which is fluorescence, or converts to a triplet state.

Triplet dye is a relatively long-lived species and has two electrons with unpaired spins. Kato et al (1963) observed triplet dye lifetimes of about thirty microseconds and Grossweiner and Zwicker

(1961) reported ten microsecond survival times. Triplet state dye either decays directly back to ground state, which is phosphorescence, or returns to ground state after transferring its energy to some other molecule. Figure 1 is a diagram of possible electronic states and transitions after light absorption by sensitizer dye.

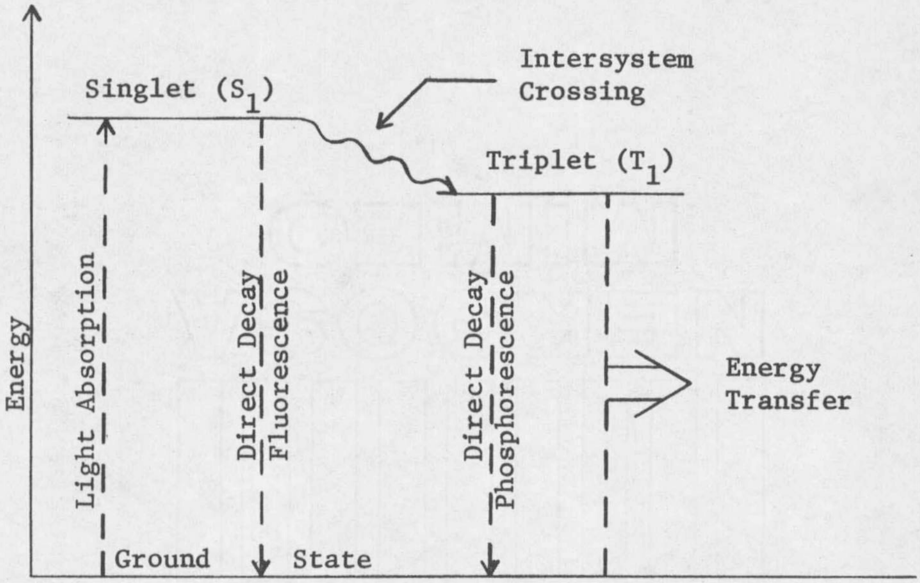


Fig. 1. ENERGY STATES AND TRANSITIONS OF SENSITIZER DYE

Energy Transfer

Final disposition of the absorbed energy of triplet dye depends on environmental conditions such as kind of solvent, type and concentration of other molecules in solution, and temperature. For energy transfer to another molecule to occur, the energy gap between ground state and the first excited state of that molecule must be less than the absorbed energy of triplet dye, which is on the order of 40 kilocalories per mole (Kcal/M) for dyes of interest as sensitizers. Most organics require much more energy to be excited than is available from triplet dye. Oxygen, however, is unusual because its ground state is a triplet and the energy gap between ground state and the first excited state, which is a singlet, is unusually low (22 Kcal/M). Hence if dissolved oxygen is present even in trace amounts triplet dye will selectively transfer its energy to oxygen. Merkel and Kearns (1972) measured quantum yields of 0.9 ± 0.1 for formation of singlet oxygen from quenching of triplet state methylene blue.

Energy transfer from triplet dye to oxygen to generate singlet oxygen is the mechanism essential to dye sensitized aerobic photooxidation. But other mechanisms can compete with and even preempt the triplet dye to oxygen energy transfer. Kepka and Grossweiner (1971) observed direct reaction between triplet eosin dye and substrate at high substrate concentration. At lower substrate concentration they found electron transfer from triplet dye to oxygen. Sargent (1971) gave a summary of other possible reaction pathways for triplet dye. Which pathway predominates is a sensitive function of at least dye concentration, electronic properties of the dye, oxygen concentration, pH, substrate concentration, and substrate reactivity.

The relative excitation energies of sensitizer dye, oxygen, and other molecules present are critical in determining the pathway of energy transfer in a dye sensitized photo-oxidation system.

Triplet Dye Energy. The triplet energy of a dye is a function of the wavelength at which the dye phosphoresces. The relationship is:

$$\lambda \times E_T = 28{,}600 \qquad (1)$$

where λ is the dye's wavelength of phosphorescence and E_T is the dye's triplet energy. From measurements of the phosphorescence wave band of a dye, its triplet energy can be calculated.

For efficient energy transfer from triplet dye to ground state oxygen, triplet dye energy should be at least 5 Kcal/M greater than the energy gap between ground state oxygen and its first singlet state (22 Kcal/M). Hence triplet dye energy should be about 27 Kcal/M or more for the dye to be capable of sensitizing singlet oxygen formation.

Energized Oxygen. Two singlet states of oxygen have been observed in aqueous dye sensitized photo-oxidation systems. The first excited state has excitation energy of 22 Kcal/M and is labeled ($^1\Delta g$). The second excited state, called ($^1\Sigma g$), has an excitation energy of 37 Kcal/M. According to Merkel and Kearns (1972) ($^1\Sigma g$) is very short-lived with an estimated lifetime of less than 10^{-4} microseconds in water. On the other hand those same investigators, in agreement with Foote (1968), estimate the lifetime of ($^1\Delta g$) to be nearly two microseconds in water. Hence ($^1\Delta g$) is probably the oxygen species involved in oxidation of substrate.

The bond electrons of ($^1\Delta g$) possess absorbed energy which has raised them to energy levels relatively more removed from the oxygen nucleus than the ground state energy levels. As a consequence those electrons, being held less tightly to the molecule, are more available for transfer to other materials. This makes the singlet state a stronger reducing agent than ground state oxygen. Conversely, since the bond electrons are relatively far from the nucleus the oxygen molecule's attraction for electrons is increased and it becomes a stronger oxidizing agent. In most reactions singlet oxygen is more likely to serve as an oxidizing agent than as a reducing agent.

Reactions of Energized Oxygen

The fate of singlet oxygen depends on the environment of the reaction system. It can be quenched by solvent, decay spontaneously to ground state, be quenched by dye or other molecules in solution, or react with substrate. The extent to which each pathway occurs is determined by such factors as sensitizer type and concentration, oxygen concentration, properties of the activating light energy, and reactivity and concentration of other molecules in solution.

Reaction between singlet oxygen and substrate is a diffusion controlled process with the rate dependent mainly on the viscosity of the solvent. According to Pitts and Calvert (1966) the rate constants for diffusion controlled bimolecular reactions are typically from 10^9 to 10^{10} liters per mole second. Quenching of singlet oxygen by dye or ground state oxygen was observed by Merkel and Kearns (1972) to be insignificant compared to quenching by water which allows a two microsecond lifetime for $(^1\Delta g)$. Hence if a reactive substrate is present the singlet oxygen-substrate reaction will likely be competitive with quenching reactions.

PROCESS PARAMETERS

Mechanisms and Reaction Conditions

There has been a great deal of controversy in the literature about reaction mechanisms which occur in a dye sensitized aerobic photo-oxidation system. Some investigators claim oxidation is by singlet oxygen. Others argue a dye-oxygen complex is the oxidizing agent. Still others are convinced ground state oxygen-substrate complex formation precedes energy transfer and oxidation. The root of controversy seems to lie in attempts by investigators to assign to all dye sensitized aerobic photo-oxidations the mechanism observed in their particular studies. More likely many mechanisms are possible depending on a multitude of parameters such as kind of sensitizer dye, properties of the light source, oxygen concentration, sensitizer concentration, pH, temperature, and concentration and reactivity of substrate. In fact a particular mechanism might be selected by proper adjustment of process parameters.

Parameter Values

A complete understanding of all parameters important in dye sensitized aerobic photo-oxidation has yet to be achieved. But there is evidence that at least pH, dye concentration, substrate concentration, properties of light source, oxygen concentration, and substrate reactivity are important.

pH. Many investigators including Weil et al (1951), Bellin and Yankus (1968), and Sargent (1971) have concluded high pH (8 to 10) favors dye sensitized aerobic photo-oxidation. Acid ionization of substrates like phenol and cresol increases electron density at the ionization site, thus enhancing attack by singlet oxygen. Also, any protons which might be liberated when substrate is oxidized are taken up by excess hydroxyl ions.

Dye Concentration. Absorption of light increases with dye concentration to the limit of available light energy. At high dye concentration, however, quenching of triplet dye by its ground state becomes important and direct reaction between sensitizer and substrate might be enhanced. Sargent (1971) concluded optimum dye concentration is on the order of 1.5×10^{-5} M for sensitizing aerobic photo-oxidation.

Substrate Concentration. Since the substrate-singlet oxygen reaction is a diffusion controlled process, increasing substrate concentration should increase reaction rate. On the other hand direct reaction between triplet dye and substrate also increases with substrate concentration. Sargent (1971) observed a cresol concentration of about 5×10^{-4} M to be optimum for methylene blue sensitized aerobic photo-oxidation.

Substrate Reactivity. Only materials reactive with singlet oxygen can be substrate for dye sensitized aerobic photo-oxidation. Substrate reactivity with triplet dye is undesirable because that reaction can result in irreversible dye destruction.

Properties of Light Source. The energy of only those light wavelengths absorbed by sensitizer dye serves to generate triplet dye and in turn singlet oxygen. The degree to which the light source emission spectrum and the sensitizer absorption spectrum overlap is a measure of total energy absorbed. For efficient use of available light energy a sensitizer should be selected to absorb as much of the light's emission spectrum as possible.

Oxygen Concentration. The relationship between triplet dye energy and the energy gap from ground state oxygen to its first singlet favors energy transfer from triplet dye to dissolved oxygen. According to Foote (1968) even trace amounts of oxygen can successfully compete for triplet dye energy.

Concentration of dissolved oxygen in water is temperature dependent and limited to about 5×10^{-4} M. If the oxygen required to oxidize substrate exceeds that value aeration is necessary. Neither oxygen concentration above trace amounts nor rate of oxygen transfer by aeration has been reported as limiting in dye sensitized aerobic photo-oxidation.

SUBSTRATE

Compounds Photo-Oxidized

According to Spikes and Straight (1967) many organic compounds including alcohols, aldehydes, amines, esters, indoles, olefins, carbohydrates, and nucleic acids can undergo sensitized photo-oxidation. Glad and Spikes (1966), Weil et al (1951) and many others have reported sensitized photo-oxidation of aromatic amino acids. Evidence that phenols and cresols can be photo-oxidized has been presented by

Grossweiner and Zwicker (1961 and 1963), Kolesnikov (1958) and Sargent (1971).

Although a wide range of compounds can be oxidized by one or another of the many photo-chemical processes, relatively few are sensitive to dye sensitized aerobic photo-oxidation. In fact Foote (1968) refers to singlet oxygen as a very selective intermediate which fails to react with most compounds. Fortunately some refractory materials like phenol, cresol, and pesticides which appear in waste streams are among those compounds reactive with singlet oxygen.

According to Craig (1972) singlet oxygen is most reactive with molecules of high electron density possessing high energy electrons. In organic compounds, unsaturated covalent bonds are sites of high electron density. But being unsaturated is not a sufficient condition for reactivity with singlet oxygen. For example benzene, with three double (pi) bonds, is electron rich but the pi bonds are evenly distributed among the carbon atoms, making the electrons quite stable. Substitution of electron withdrawing groups like nitro, sulfo, or cyano groups reduces the pi bond density in the benzene ring and makes the aromatic even more difficult to oxidize. On the other hand if electron donating groups like hydroxyl or methyl groups are substituted, the pi bond density at the ring carbon atoms increases and the resulting aromatic is more susceptible to oxidation.

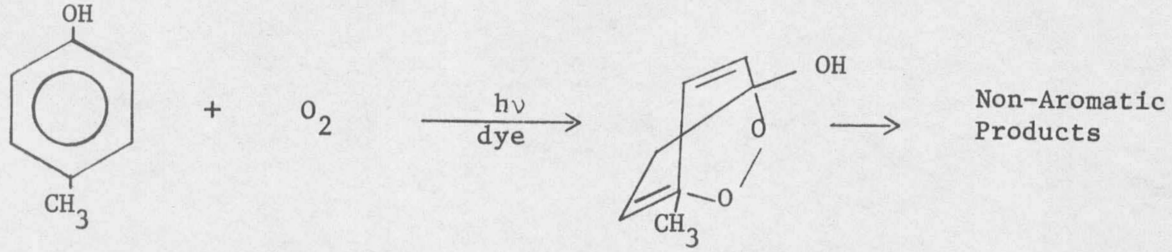
Cresol, with one hydroxyl and one methyl group substituted on a benzene ring, should be reactive with singlet oxygen. Sargent (1971) observed a cresol half-life of less than ten minutes in a dye sensitized aerobic photo-oxidation system. Similarly phenol and the aromatic amino acids have proved sensitive to oxidation by singlet oxygen.

The aromatic ring is the structure in many organics which makes them refractory to most wastewater treatment processes, especially biological oxidation. Since singlet oxygen will readily react with many substituted aromatic molecules, dye sensitized aerobic photo-oxidation might be applied to waste treatment.

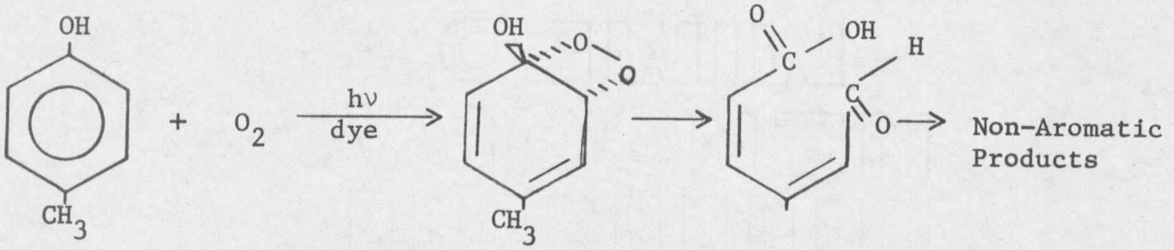
Oxidation Products

The greatest potential for dye sensitized aerobic photo-oxidation applied to waste treatment probably lies in destruction of unsaturated heterocyclic compounds. Therefore only products of reaction between singlet oxygen and aromatic ring structures are discussed here.

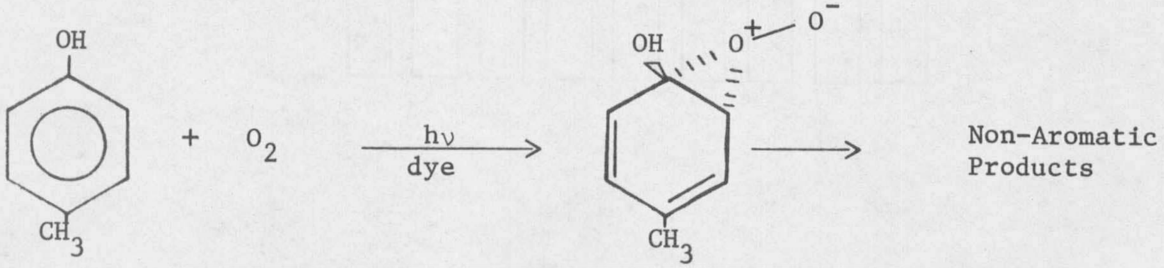
Craig (1973) suggests three possible pathways by which singlet oxygen might react with unsaturated heterocyclic compounds. For convenience they are labeled Diels-Alder reaction, dioxetane ring mechanism, and ene reaction. The three pathways are illustrated in Figure 2 for the reaction of singlet oxygen with cresol. The super-epoxide reaction shown in Figure 2 is an alternate of the dioxetane ring mechanism wherein only one atom of the oxygen molecule bonds to two adjacent carbon atoms in cresol's benzene ring. Which pathway



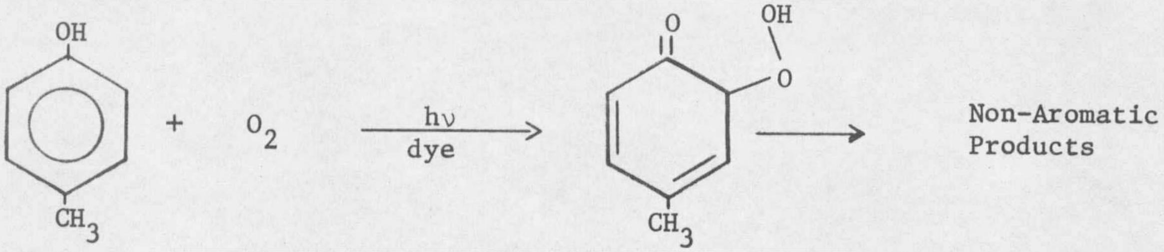
Diels - Alder Reaction



Dioxetane Ring Mechanism



Super - Epoxide Reaction



Ene Reaction

Fig. 2. POSSIBLE PATHWAYS FOR REACTION OF CRESOL WITH SINGLET OXYGEN

predominates in a given reaction system has yet to be determined. But regardless of mechanism a primary consequence of the cresol-singlet oxygen reaction is the opening of cresol's aromatic ring. With the ring open the oxidation products are likely to be tractable to biological oxidation.

SENSITIZER

Definition

For the purposes of this discussion the sensitizer is a dye which absorbs visible light energy, transfers it to dissolved oxygen, then returns to ground state to absorb more light. According to this definition a dye involved in electron transfer, hydrogen transfer, complex formation, free radical formation, or any other reaction besides energy transfer is not a true sensitizer.

Many substances including chlorine, ferrous and ferric iron, zinc, titanium dioxide, sand and various organic molecules have been referred to as sensitizers for photo-oxidation. In the photo-chemical processes involving chlorine studied by Hancil and Smith (1971) and many others the chlorine molecules probably break into chloride radicals after light absorption. Chloride radical, a strong oxidizing agent, is then consumed in oxidizing substrate. But since there is net loss of chlorine it is not a true sensitizer. Similarly ions of metals like iron and zinc have been called photo-sensitizers in reports by Matsuura and

Smith (1970) and Kinney and Ivanuski (1969) and others. But metal ions probably enhance substrate oxidation by electron transfer from hydroxyl ion to metal ion to form hydroxide radical, a strong oxidizing agent. Hence the metal ions are primary reactants rather than sensitizers.

Many dyes have proved capable of sensitizing aerobic photo-oxidation using visible light. Blum (1941) reported Rose Bengal, methylene blue, and neutral red were effective sensitizers. Yamamoto (1958) successfully used azur I, methylene blue, brilliant cresyl blue, toluidine blue, and acridine orange as sensitizers of aerobic photo-oxidation. Bellin and Oster (1960) used methylene blue, fluorescein, thioflavin, proflavin, neutral red, hematoporphyrin, and Rose Bengal.

Dye Photo-Reduction

According to Koizumi et al (1963) some sensitizer dyes in water solution are slowly photo-reduced by visible light with no substrate present. Those authors state the mechanism of dye photo-reduction is not well understood, but speculate that electron transfer between triplet dye and ground state dye, and demethylation of dye are possible. The reduced dye is colorless (bleached) and is no longer a sensitizer for singlet oxygen formation. Many photo-reduced dyes will recover their color and sensitizing ability during a period of aeration with no illumination.

Dye Application

The sensitizer dyes are relatively expensive as water or wastewater treatment chemicals. Although only about 10^{-5} M dye concentration is required, sensitizer will probably have to be recovered and reused several times for the process to prove economical as a waste treatment method. Also, since the dyes have great tinctorial strength they would have to be removed from the waste stream being treated to prevent objectionable color.

The most promising method of dye application and recovery involves attaching the sensitizer to high molecular weight polymers like ion exchange resins, polysaccharides, or polymeric gels. The dye can serve as sensitizer while attached to the polymer and then be removed with the polymer by sedimentation, screening, or some other process. A fixed bed process similar to traditional ion exchange might also be possible.

Many investigators including Bradley and Wolf (1959), Vitagliano and Costantino (1970), Bellin and Yankus (1968) and Axen et al (1967) have successfully attached organic molecules, including dyes, to polymers by methods which leave the attached molecules capable of participating in various chemical processes. In fact Kautsky (1938) observed oxidation of substrate by dye sensitized aerobic photo-oxidation when both dye and substrate were attached to solid silica gel. And Seely

(1973) was able to photo-oxidize chlorophenol using a sensitizer dye attached to a polysaccharide.

The influence of dye binding on its ability to sensitize aerobic photo-oxidation is not well understood. According to Kautsky (1938) and Bellin (1968) an increase in quantum yield of singlet oxygen might be expected from bound dye because: (1) if binding to polymer results in dye aggregation the energy required for electron excitation is lowered, and (2) triplet dye production is greater in bound than in dispersed systems. On the other hand Bellin and Yankus (1968) observed a quantum yield for tyrosine degradation sensitized by bound methylene blue much lower than that obtained with dye in dispersed solution. Bellin (1968) speculated bound dye molecules were protected from interaction with oxygen by enfolding polymer chains and by increased viscosity in the polymer's micro-environment.

If an opaque polymer is used, some portion of the bound dye might be in the shadow of polymer. The importance of this shadow effect in reducing light absorption probably depends on the concentration of polymer and dye and the degree of mixing. The shadow effect has not yet been reported as a major cause of decreased reaction rate with polymer-bound dye.

Evidently further study is needed to develop a dye application and recovery method which allows efficient production of singlet oxygen but permits little loss or destruction of dye.

CHAPTER III

EQUIPMENT AND MATERIALS

MATERIALS

DYES

Dyes tested for effectiveness as sensitizers for dye sensitized aerobic photo-oxidation were rhodamine 6G, sodium phthalocyanine, 2,7-dichlorofluorescein, neutral red, methylene blue, Rose Bengal, malachite green, hematoporphyrin-D,L-hydrochloride, and acridine orange. Stock dyes were reagent grade obtained from various suppliers of laboratory chemicals.

Absorption peaks in the visible spectrum (4200-6600 A°) for the dyes tested are shown in Table I. Na-phthalocyanine is insoluble enough in water that an absorption spectrum for dissolved dye cannot be readily measured. The absorption spectrum for hematoporphyrin-D,L-hydrochloride in water has three peaks of nearly equal height between 4750 and 6000 A° with the maximum peak occurring at 5200 A°.

SUBSTRATES

Para-cresol ($CH_3C_6H_4OH$) and phenol (C_6H_5OH) were tested for reactivity with singlet oxygen in a dye sensitized aerobic photo-oxidation system. Stock chemicals were reagent grade from J. T. Baker company and were used without further purification.

TABLE I

SENSITIZER DYE ABSORPTION PEAKS

Dye	Absorption Peak (A°)
Rhodamine 6G	5250[a]
2,7-dichlorofluorescein	5110[b]
Neutral red	4540[a]
Methylene blue	6650[a]
Rose Bengal	5500[a]
Malachite green	6180[a]
Acridine orange	5390[b]

[a] Gurr (1971)

[b] Chambers and Kearns (1969)

BUFFERS

Table II shows the materials used to buffer solutions as required for this study.

RESINS

Methylene blue was bound to several commercially available ion exchange resins to determine the effect of binding on the dye's

TABLE II

BUFFER MATERIALS

pH	Buffer Materials[a]
5	KH_2PO_4 (0.03 M) plus NaOH
6	KH_2PO_4 (0.03 M) plus NaOH
7	Trizma[b] (0.008 M) plus HCl
8	Trizma (0.008 M) plus HCl
9	Boric acid (0.01 M), Trizma (0.008 M) plus HCl, $NaHCO_3$ (0.01 M) plus NaOH
10	$NaHCO_3$ (0.01 M) plus NaOH

[a] reagent grade

[b] tris(hydroxymethyl)aminomethane

ability to sensitize singlet oxygen formation. The names, size ranges, and ionic forms of resins tested are shown in Table III.

Resins were obtained from the various suppliers of commercial ion exchange resins.

TABLE III

DYE-BINDING RESINS

Resin	Ionic Form	Mesh Size
Duolite C-20X4	Strong acid-hydrogen form	40-80
Dowex HCR	Strong acid-sodium form	20-50
Duolite ES-80	Weak acid-hydrogen form	16-50
Duolite C-25D	Strong acid-sodium form	16-50
Powdex (PCH)	Strong acid-hydrogen form	200-400

EQUIPMENT

REACTOR

The reactor shown in Figure 3 was specially designed and fabricated for use in this investigation.

The cooling water jacket, outer wall, and inner cylinders are of cast acrylic tubing with 1/4 inch wall thickness. Four inner cylinders with outside diameters of four, five, six, and seven inches can be interchanged to vary the thickness of the liquid layer.

Both fluorescent and tungsten incandescent lamps were tested as light sources for dye sensitized aerobic photo-oxidation. In Figure 3 the reactor is equiped with Sylvania CWD, 300 watt tungsten incandescent

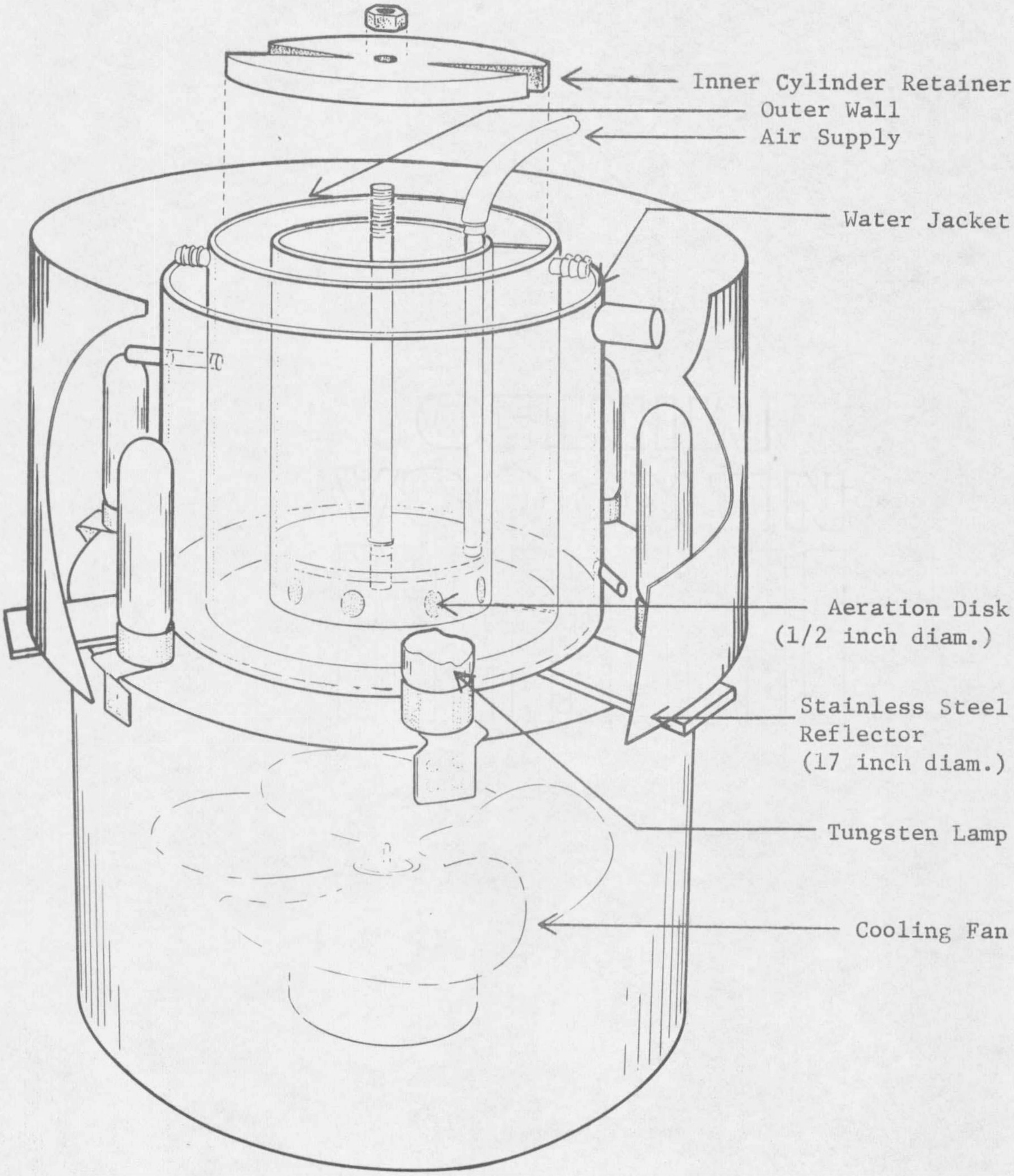


Fig. 3. REACTOR EQUIPPED WITH TUNGSTEN LAMPS

projector lamps. To vary light intensity in the reactor, cylindrical screens to slide over each of the six lamps were made from 1/16 inch mesh aluminum, 1/4 inch mesh galvanized, and 1/4 inch mesh copper screen.

Figure 4 shows the reactor equipped with twelve inch diameter circline fluorescent lamps. They are 40 watt daylight fluorescent lamps, General Electric number FC12T10D. The fluorescent lamps were tested with no cooling water jacket on the reactor.

The cooling fan is a Dayton fourteen inch furnace duct fan. Solutions in the reactor were aerated from a filtered, oil pumped air supply.

LIGHT INTENSITY

An Isco model SR spectroradiometer equipped with a remote sensing probe was used to measure light intensity in the reactor.

SUBSTRATE CONCENTRATION

Cresol and phenol concentrations were measured with a Varian Aerograph model 204 1B dual channel gas chromatograph with flame ionization detectors. The operating parameters for gas chromatographic measurement of cresol and phenol are shown in Table IV. The same operating conditions were used for both substrates.

The output of the gas chromatograph was recorded with a Sargent model DSRG dual channel recorder operating at 1 micro-volt for full span.

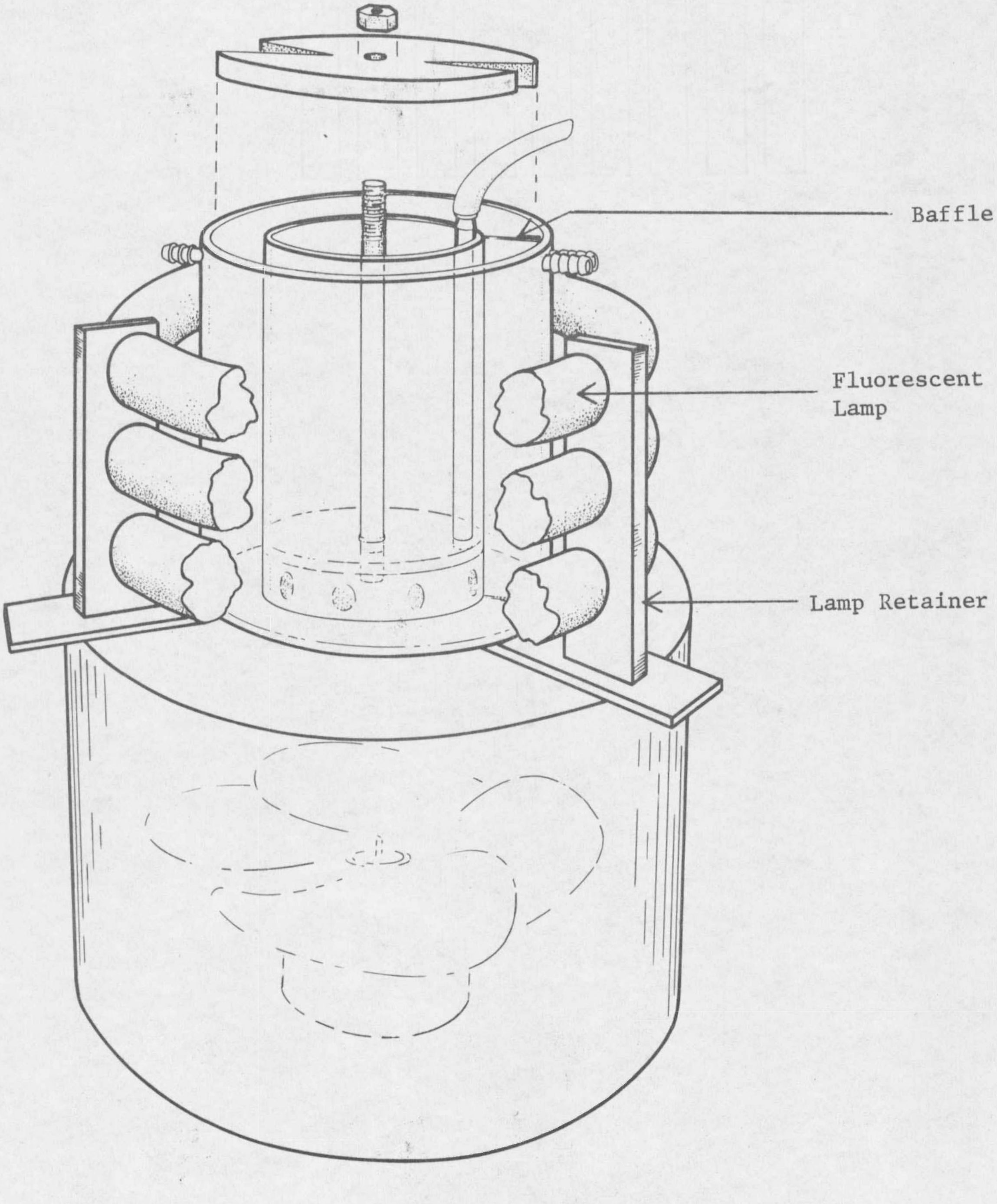


Fig. 4. REACTOR EQUIPPED WITH FLUORESCENT LAMPS

TABLE IV

OPERATING CONDITIONS FOR GAS CHROMATOGRAPHIC MEASUREMENT OF CRESOL AND PHENOL

Parameter	Description
Support material	60/80 Chromosorb W, AW-DMCS
Stationary phase (liquid)	15% FFAP (free fatty acid phase)
Column-	
a) Material	a) Stainless steel
b) Diameter	b) 1/8 inch
c) Length	c) 5 feet
Column oven temperature	200°C
Detector temperature	237°C
Injector temperature	220°C
Sample size	2 micro-liters
Carrier gas	Helium @ 65 psig
Carrier flow	38 ml/min
Detention times	Phenol - 6 min Cresol - 7.5 min

HYDROGEN ION CONCENTRATION

pH measurements were made with a Corning model 12 research pH meter equipped with a Sargent model S-30072-15 combination electrode.

DYE CONCENTRATION

A Bausch and Lomb Spectronic 20 spectrophotometer was used to monitor dye concentration and dye bleaching. For each dye, measurements were made at the wavelength of peak absorption given in Table I.

FLUORESCENCE

Rhodamine B was used in a washout study of the reactor to determine mixing characteristics. Fluorescence from Rhodamine B was measured with a G. K. Turner model 111 fluorometer.

DISSOLVED OXYGEN

Dissolved oxygen concentration was measured with a YSI model 54 dissolved oxygen meter equipped with a Sargent model 5419 remote sensing probe.

CHAPTER IV

PROCEDURE

FLUORESCENT LAMPS

LIGHT PROPERTIES

The spectroradiometer used to measure light intensity gives a spectral intensity reading in micro-watts per square centimeter per millimicron wave band ($\mu w/cm^2/m\mu$) for any selected wavelength. Intensity readings were taken for wavelengths from 400 mμ to 750 mμ at 25 mμ intervals. A plot of one set of intensity readings taken over the range of wavelengths is an emission spectrum (see Figure 5).

Since light intensity varies from place to place in the reactor six emission spectra were measured and combined into one representative spectrum for the fluorescent lamps. The spectroradiometer probe was held flat against the outer reactor wall facing the lamps for all six spectrum measurements. Spectra were measured at the bottom of the reactor, directly opposite each of the three lamps, halfway between the bottom and middle lamps, and halfway between the middle and top lamps. An average emission spectrum was obtained by averaging the six different intensity readings at each measured wavelength. The measured intensities varied by as much as 38 percent from the average spectrum.

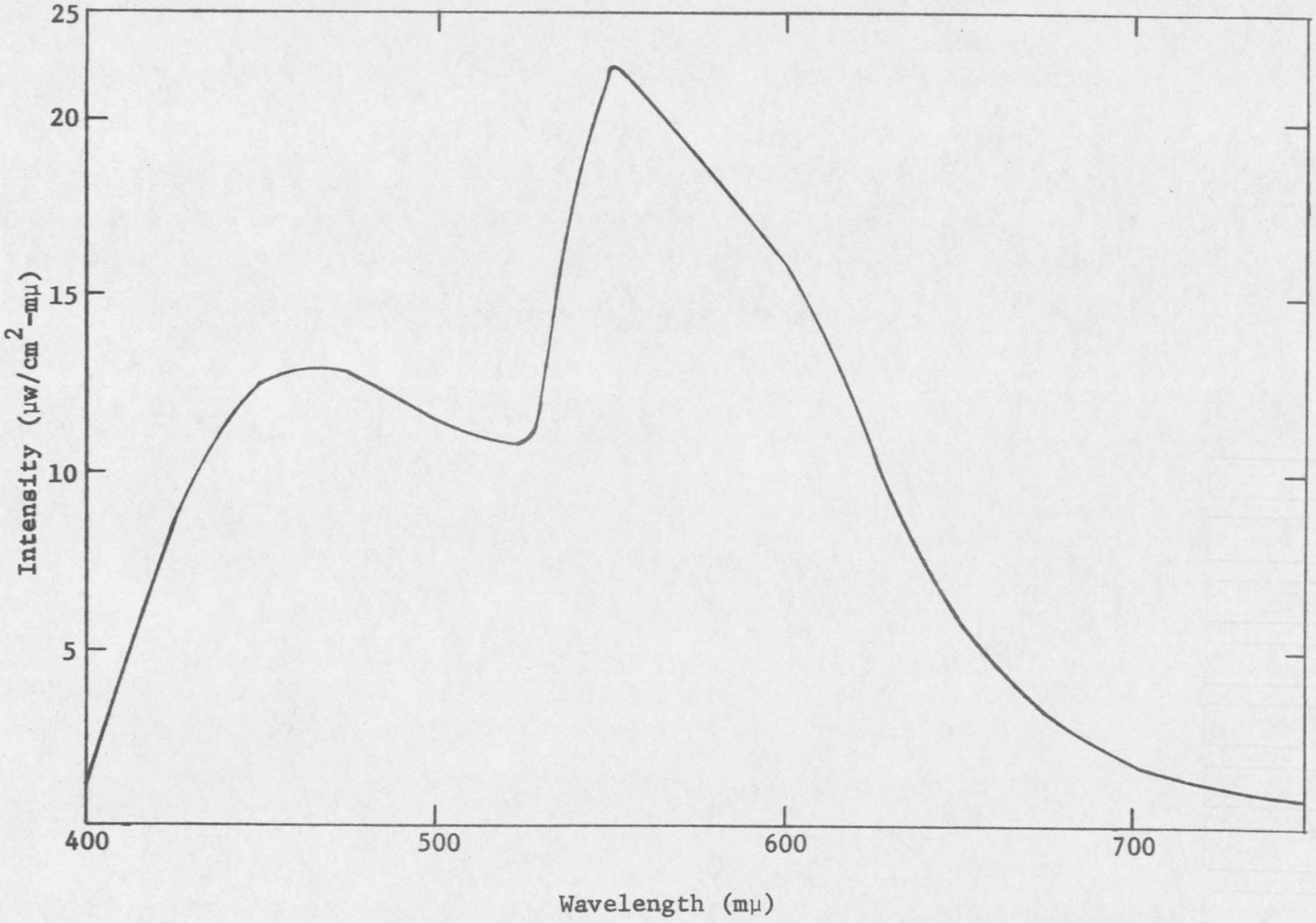


Fig. 5. AVERAGE EMISSION SPECTRUM FROM FLUORESCENT LAMPS IN REACTOR

CONCENTRATIONS

Several dyes at various concentrations were tested in the reactor shown in Figure 4 for ability to sensitize aerobic photo-oxidation of cresol using daylight fluorescent lamps. Liquid layer thickness of reaction solution was 3/4 inch for this and all succeeding experiments unless otherwise specified. Dyes tested were methylene blue at 1,5 and 10 mg/l; 2,7-dichlorofluorescein at 5 and 10 mg/l; rhodamine 6G at 5 mg/l; and neutral red in saturated solution. Na-phthalocyanine, a dye relatively insoluble in water, was tested by adding 40 mg of dye powder to 800 ml of aqueous reaction solution. The resulting mixture contained both dye in solution and undissolved dye. Cresol concentration was 50 mg/l in all tests.

Eight-hundred milliliters of each dye-cresol combination were buffered at pH 9 and poured into the aerated reactor. A 5 ml sample was taken before the lamps were turned on. After illumination began, 5 ml samples were taken at five minute intervals for a total of 30 minutes. Each sample was tested for pH, cresol concentration, and dye bleaching. A spectrophotometer was used to measure loss of color by dye due to bleaching.

TUNGSTEN LAMPS

Since little substrate oxidation was achieved in the reactor of Figure 4 using fluorescent lamps, the reactor was modified to accommodate tungsten incandescent lamps as shown in Figure 3. A cooling water jacket was placed between the tungsten lamps and the test solution. In addition a stainless steel reflector was placed around the lamps.

LIGHT PROPERTIES

Lamps Unscreened

Sixteen emission spectra were measured and combined into a single spectrum representative of average light intensity in the reactor equipped with tungsten lamps. All sixteen spectra were measured with the spectroradiometer probe held against the reactor outer wall facing the lamps and reflector. A spectrum was measured directly opposite each lamp at two inches above the reactor bottom. A spectrum was also measured midway between each adjacent pair of lamps at two inches above the reactor bottom. In addition, spectra were measured directly opposite one of the lamps (designated L_1) at 1 and 3 1/2 inches above the reactor bottom, and midway between an adjacent pair of lamps (designated L_1 and L_2) at 1 and 3 1/2 inches above the reactor bottom. Three and one-half inches is the depth of reaction solution in the reactor of Figure 3 when the liquid layer thickness is 3/4 inch.

The sixteen spectra were combined into one representative spectrum as follows:

1. An average emission spectrum at two inches above the reactor bottom was obtained by averaging the twelve intensities measured for each wavelength at two inches

above the reactor bottom. These average intensities are labeled $E_{2'',\lambda}$ where λ is the measured wavelength.

2. An average emission spectrum opposite lamp L_1 was obtained by averaging the three intensities measured opposite the lamp at each wavelength. These average intensities are labeled $E_{L_1,\lambda}$.
3. An average emission spectrum midway between lamps L_1 and L_2 was obtained by averaging the three intensities measured between those two lamps at each wavelength. These average intensities are labeled $E_{L_1L_2,\lambda}$.
4. Dividing $E_{L_1,\lambda}$ by the intensity at each wavelength measured opposite lamp L_1 and two inches above the reactor bottom gives a fraction arbitrarily called $f_{1,\lambda}$ for each wavelength. Similarly, dividing $E_{L_1L_2,\lambda}$ by the intensity at each wavelength measured between lamps L_1 and L_2 and two inches above the reactor bottom gives a fraction labeled $f_{2,\lambda}$ for each wavelength.
5. The average intensity in the reactor at each wavelength was calculated using the formula:

$$\text{average } I_\lambda = E_{2'',\lambda} \times \frac{(f_1 + f_2)}{2} \qquad (2)$$

Intensities measured opposite one of the lamps at two inches above the reactor bottom varied by as much as 100 percent from the average spectrum. The remaining measured intensities varied by less than 40 percent of the average spectrum.

Lamps Screened

To vary light intensity in the reactor, cylindrical wire mesh screens were placed over each lamp. Three levels of light intensity were obtained with the following screening conditions: (1) a 1/16 inch mesh aluminum screen over each lamp, (2) a 1/4 inch mesh galvanized screen over each lamp, and (3) a 1/4 inch mesh copper plus a 1/16 inch mesh aluminum screen over each lamp.

For each screening condition an average emission spectrum was obtained as described in the previous section. The variation of measured intensities from the average spectrum was similar to the variation with unscreened lamps.

DYES

Cresol Substrate

Several dyes at concentration 5 mg/1 were tested for ability to sensitize aerobic photo-oxidation of 50 mg/1 cresol using light energy from tungsten incandescent lamps. Dyes used were methylene blue, hematoporphyrin-D,L-hydrochloride, and acridine orange. Eight-hundred milliliters of dye-cresol solution were buffered at pH 9 and poured into the aerated reactor of Figure 3. A 5 ml sample was taken before turning on the light and after 1,2,3,4,5 and 10 minutes of illumination. Each sample was tested for pH, cresol concentration, and dye bleaching.

Phenol Substrate

Methylene blue, hematoporphyrin-D,L-hydrochloride, Rose Bengal, acridine orange, 2,7-dichlorofluorescein, malachite green, and rhodamine 6G were dyes tested at 5 mg/1 for ability to sensitize aerobic photo-oxidation of 50 mg/1 phenol using tungsten lamps. Experimental procedure was the same as that described in the previous section for testing the various dyes with cresol.

OPTIMIZING PROCESS PARAMETERS

In all experiments for optimizing process parameters 800 ml of the various solutions being tested were poured into the aerated reactor. A 5 ml sample was taken before turning on the lamps and after 1,2,3,4,5 and 10 minutes of illumination. Each sample was tested for pH, substrate (cresol) concentration, and dye bleaching.

Hydrogen Ion Concentration

The aerobic photo-oxidation rate of 50 mg/1 cresol sensitized by 5 mg/1 methylene blue was optimized for pH in the range of pH 5 to 10. Dye-cresol solutions were buffered to pH's 5,6,7,8,9 and 10 using the buffer materials listed in Table II.

An unbuffered solution of 50 mg/l cresol with 5 mg/l methylene blue was aerated and illuminated for ten minutes to test reaction rate in unbuffered solution.

Buffer Dependence. Fifty milligrams per liter cresol and 5 mg/l methylene blue were tested at pH 9 using three different buffer systems to determine the dependence of reaction rate on chemical properties of the different buffers. The three buffer systems used are listed in Table II.

Base Dependence. A reaction is general base dependent if its rate is a function of the total amount of basic buffer material present in solution. General base dependence is not the same as pH dependence. The same pH can be maintained with different quantities of the same basic buffer material. Only the buffer capacity changes. Hence a general base dependent reaction has its reaction rate dependent upon the buffer capacity of a given buffer system.

To determine if the methylene blue-cresol aerobic photo-oxidation process is general base dependent, 50 mg/l cresol and 5 mg/l dye were tested in solutions buffered at pH 9 with four different capacities of $NaHCO_3$ and NaOH. The concentrations of $NaHCO_3$ and NaOH used to obtain the four different buffer capacities are listed in Table V.

TABLE V

BUFFER SYSTEMS FOR TESTING GENERAL BASE DEPENDENCE

Buffer System	$NaHCO_3$ (moles/l)	NaOH (moles/l)
1	$1x10^{-6}$	$5x10^{-4}$
2	$1.2x10^{-5}$	$1x10^{-3}$
3	$1.6x10^{-5}$	$3x10^{-3}$
4	$6x10^{-5}$	$5x10^{-3}$

Dye Concentration

To determine optimum sensitizer concentration, methylene blue concentrations of 1,3,5,7,10 and 15 mg/l were used to sensitize aerobic photo-oxidation of 50 mg/l cresol. The dye optimization tests were run at pH 9 since earlier experiments for optimizing pH showed pH 9 was favorable for the process. The buffer system was 1.2×10^{-5} M $NaHCO_3$ with 1.0×10^{-3} M NaOH.

Substrate Concentration

Cresol concentrations of 20,50,100,200 and 300 mg/l were sensitized by 5 mg/l methylene blue for aerobic photo-oxidation to determine optimum substrate concentration. Five milligrams per liter was the optimum dye concentration from tests for optimizing sensitizer concentration described in the previous section. These experiments were run at pH 9 with a 1.2×10^{-5} M $NaHCO_3$ plus 1.0×10^{-3} M NaOH buffer system.

Liquid Layer Thickness

Thickness of the liquid layer of solution being tested in the reactor of Figure 3 can be varied by interchanging inner wall cylinders. Liquid layers of 1/4, 3/4, 1 1/4, and 1 3/4 inches can be obtained.

Solutions of 100 mg/1 cresol and 5 mg/1 methylene blue buffered at pH 9 with 1.2×10^{-5} M $NaHCO_3$ and 1.0×10^{-3} M NaOH were tested for rate of aerobic photo-oxidation at each liquid layer thickness. Fifty milligrams per liter was the optimum cresol concentration from tests for optimum substrate concentration described in the previous section. But a cresol concentration of 100 mg/1 was used because it represents higher concentrations which might be expected in a waste stream.

Different volumes of reaction solution are required to fill the reactor to the same level at the various thicknesses of liquid layer. Table VI lists the volume of solution for each liquid layer thickness.

Light Intensity

The tungsten lamps were screened as described earlier to obtain four levels of light intensity in the reactor: (1) full intensity with no screens, (2) 86 percent of full intensity with 1/4 inch mesh

TABLE VI

REACTION SOLUTION VOLUMES REQUIRED AT EACH LIQUID LAYER THICKNESS

Liquid Layer Thickness (inches)	Volume (ml)
1/4	280
3/4	800
1 1/4	1230
1 3/4	1590

galvanized screens, (3) 79 percent of full intensity with 1/16 inch mesh aluminum screens, and (4) 54 percent of full intensity with the combination of 1/4 inch mesh copper and 1/16 inch mesh aluminum screens.

Solutions of 100 mg/l cresol and 5 mg/l methylene blue buffered at pH 9 with 1.2×10^{-5} M $NaHCO_3$ and 1.0×10^{-3} M NaOH were tested at each level of light intensity.

Dye Photo-Reduction

If sensitizer is being photo-reduced while sensitizing aerobic photo-oxidation of substrate, an increase in reaction rate might be expected if periods of illumination are interspersed with periods of no light during which dye can recover from photo-reduction. A test of aerobic photo-oxidation rate of 100 mg/l cresol sensitized by 5 mg/l methylene blue was run with one minute illumination periods separated by one minute periods of no light. Total illumination time was ten minutes and 5 ml samples were taken after 1,2,3,4,5 and 10 minutes of illumination. The reaction was buffered at pH 9 with 1.2×10^{-5} M $NaHCO_3$ and 1.0×10^{-3} M NaOH.

FLOW-THROUGH REACTION

The reactor shown in Figure 3 has an inlet and outlet to allow testing dye sensitized aerobic photo-oxidation in flow-through process. The outlet is located to maintain 800 ml of solution in the reactor with the six inch inner cylinder in place.

Solutions of 100 mg/l cresol and 5 mg/l methylene blue buffered at pH 9 with 1.2×10^{-5} M $NaHCO_3$ and 1.0×10^{-3} M NaOH were pumped through the reactor at rates of 115,170, and 225 ml/min. Detention times in the reactor for those pumping rates are 6.96,4.71 and 3.55 minutes respectively. In each of the flow-through experiments the lamps were turned on after discharge from the reactor outlet was steady at the desired rate. Five milliliter samples were taken after 10,20 and 30 minutes of illumination. Each sample was tested for pH, cresol concentration, and dye bleaching.

DYE BINDING

Attaching Dye to Resin

Each of the five ion exchange resins listed in Table III was coated with methylene blue dye. Before being coated the resins were washed with distilled water for several hours. Two-hundred milliliters of each wet, washed resin were added to 250 ml of 6 mg/l methylene blue solution at pH 9 and 22.5°C, mixed for several minutes, and allowed to sit for about twelve hours. Then the resin was screened from remaining dye solution with a 100 mesh per inch screen. After screening, the dye coated resin was washed with distilled water for one hour.

Duolite C-20X4 resin was coated with varying amounts of dye. One-hundred milliliter volumes of wet resin were added to 200 ml of six different strengths of dye solution at pH 9 and 22.5°C and mixed for ten minutes. Dye solutions were 20,150,350,500,5000 and 25000 mg/l. Coated resin was then screened from remaining dye solution and washed with distilled water. Concentration of dye remaining in each coating solution after resin removal was measured with a spectrophotometer.

Duolite C-20X4 resin was also coated with methylene blue by pumping 0.5 percent dye solution through a 100 ml volume of resin until dye breakthrough occurred. Pumping rate was about 100 ml/min. After breakthrough the coated resin was washed for one hour with distilled water.

Testing Bound Dye

Resin-bound dye was tested for ability to sensitize aerobic photo-oxidation of 100 mg/l cresol in batch process at pH 9 buffered with 1.2×10^{-5} M $NaHCO_3$ and 1.0×10^{-3} M NaOH. One-hundred milliliters of dye-coated wet resin were put in the aerated reactor with enough buffered cresol solution to make 800 ml of reaction solution. A sample was taken before turning on the lamps and after 2,4,6,8,10 and 20 minutes of illumination. Each sample was tested for pH, cresol concentration, and dye released by resin.

REACTIONS WITHOUT SINGLET OXYGEN

Light energy and dye to absorb the light energy must be present if singlet oxygen is to be produced from ground state oxygen in solution. Any substrate destruction occurring with light, dye, or dissolved oxygen absent is not due to oxidation by singlet oxygen.

To measure cresol destruction not attributable to oxidation by singlet oxygen, the following tests were performed:

1. A solution of 50 mg/l cresol buffered at pH 9 and containing no dye was illuminated and aerated for ten minutes.
2. In a solution swept by nitrogen to make it anaerobic and buffered at pH 9, 50 mg/l cresol with 5 mg/l methylene blue were illuminated for ten minutes in the reactor.

3. A solution of 50 mg/l cresol and 5 mg/l methylene blue buffered at pH 9 was aerated in the reactor for ten minutes with no illumination.

Cresol disappearance during tests with resin-bound dye might be due partially to ion exchange or adsorption on the resin. To determine cresol disappearance not caused by singlet oxygen oxidation, 100 ml of each resin listed in Table III were added to a solution of 50 mg/l cresol buffered at pH 9 and aerated and illuminated for ten minutes.

MIXING

Mixing characteristics of the reactor were checked by performing a washout study with rhodamine B dye. Ten milliliters of 6.25 mg/l rhodamine B in distilled water were poured into the reactor as an instantaneous slug at the inlet. With time of dye addition as time zero, samples were taken at the reactor outlet at times 10,20,30,40 and 50 seconds; and 1, 1 1/2, 2, 2 1/2, 3, 3 1/2, 4 and 4 1/2 minutes. The flow rate was 160 ml/min. Each sample was analyzed for relative fluorescence from rhodamine B.

OXYGEN TRANSFER

The rate of oxygen transfer from air to solution in water in a reactor has traditionally been considered a first-order process. The first-order rate constant is called the oxygenation coefficient for the reactor.

Eight-hundred milliliters of water containing 1.0 mg/l dissolved oxygen were added to the aerated reactor shown in Figures 3 and 4. The water was deoxygenated from near saturation to 1.0 mg/l by boiling. The air diffusers shown in Figures 3 and 4 are 1/8 inch thick polypropylene disks with 45 micron pores. The aeration rate was fast enough to insure good mixing and make it visibly evident air bubbles were dispersed throughout the solution, but not so fast as to expel solution from the reactor. With time of water addition as zero, 25 ml samples were taken and analyzed for dissolved oxygen at times 1,2,3,4 and 5 minutes.

DATA ANALYSIS

Chromatograms

Cresol concentration was measured by correlating chromatogram peak area with the concentration of cresol in standards. Peak area was estimated by multiplying peak height times peak width at 1/2 peak height. Peak areas calculated by this method are within three percent of the actual area.

Reaction Rate

Rate of dye sensitized aerobic photo-oxidation in this study is described by the rate of decline in substrate concentration. The substrate disappearance data for each experiment were fitted by the method of least squares to the equation:

$$C = C_o e^{kt} \tag{3}$$

where C is substrate concentration at time t, C_o is initial substrate concentration at t = 0, t is elapsed time, and k is a first-order reaction rate constant.

A digital computer performed the least squares curve-fit procedure and listed the rate constant for each experiment. A computerized error analysis was also made listing the percent by which the data deviated from the fitted curves. A sample of the computer printout is shown on page 101 of the appendix.

CHAPTER V

RESULTS

LIGHT SOURCE

Figure 5 is the emission spectrum representative of light impinging on the outer wall of the reactor in Figure 4.

Light conditions at the outer wall of the reactor equipped with unscreened tungsten lamps are described by the emission spectrum in Figure 6.

Three different light intensities were obtained in the reactor by putting various screens over the tungsten lamps. Figure 7 shows the emission spectra for the various screening conditions.

DYES

FLUORESCENT LAMPS

Very little aerobic photo-oxidation of cresol was observed in tests using fluorescent lamps. The first-order reaction rate of cresol disappearance was virtually zero with Na-phthalocyanine, rhodamine 6G, and neutral red as sensitizers. The 2,7-dichlorofluorescein sensitized rate constant was -0.003 min^{-1} for 5 mg/l dye and -0.004 min^{-1} for 10 mg/l dye. Rate constants with methylene blue were -0.011, -0.016 and -0.014 min^{-1} for dye concentrations of 1,5 and 10 mg/l respectively.

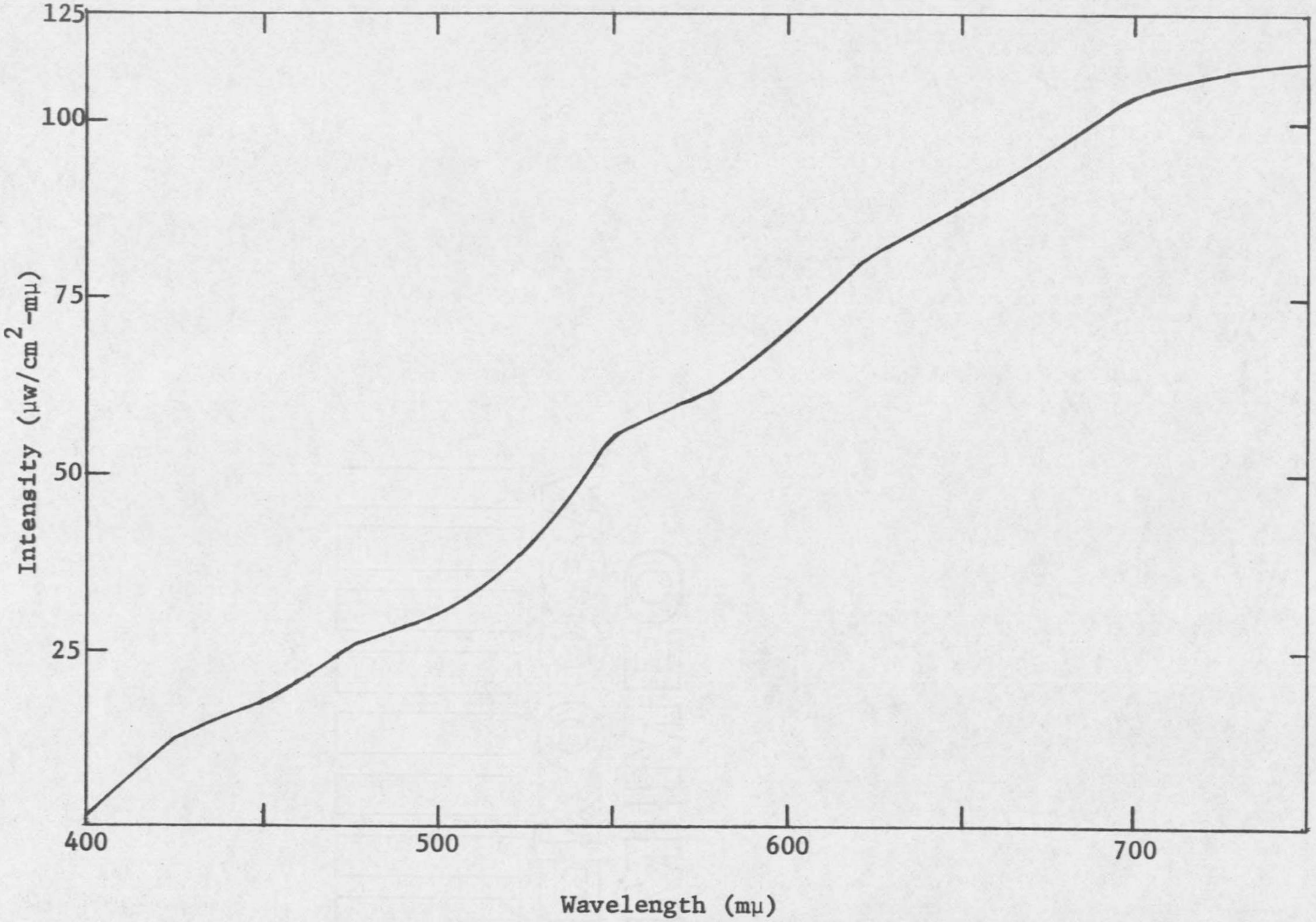


Fig. 6. AVERAGE EMISSION SPECTRUM FROM UNSCREENED TUNGSTEN LAMPS IN REACTOR

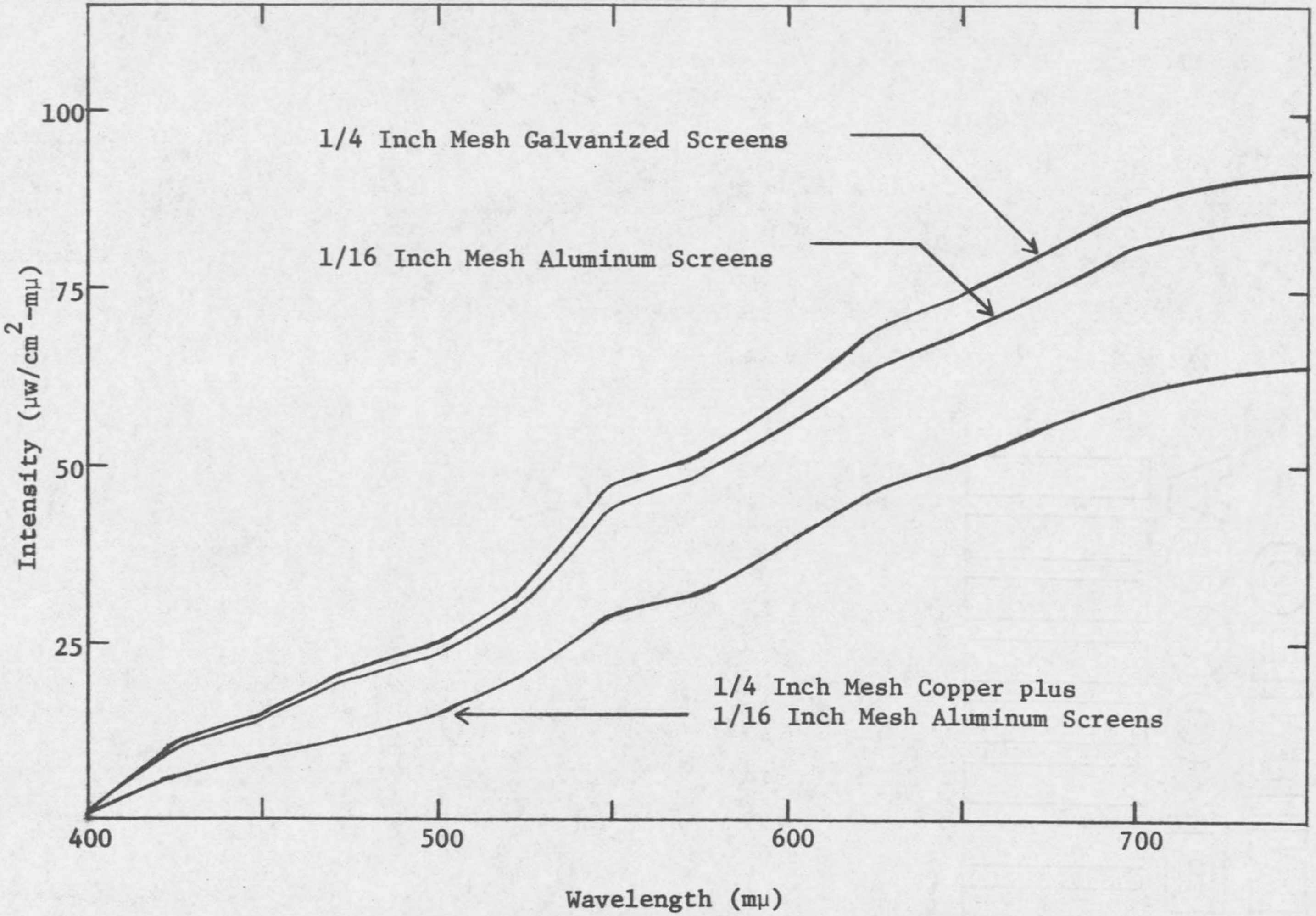


Fig. 7. AVERAGE EMISSION SPECTRA IN REACTOR WITH SCREENED TUNGSTEN LAMPS

TUNGSTEN LAMPS

Phenol

Aerobic photo-oxidation of 50 mg/l phenol using tungsten lamps was negligible when sensitized by 5 mg/l 2,7-dichlorofluorescein.

Data from experiments with acridine orange, malachite green and rhodamine 6G are scattered and not well described by the first-order kinetics equation. However, little phenol destruction was observed. Phenol concentration went from 50 to about 42 mg/l after ten minutes of illumination and aeration with each of the three dyes.

With methylene blue, hematoporphyrin-D,L-hydrochloride, and Rose Bengal as sensitizers phenol destruction rate constants were -0.100, -0.045 and -0.092 min^{-1} respectively.

Cresol

All dyes tested proved capable of sensitizing measurable aerobic photo-oxidation of 50 mg/l cresol. Table VII lists the first-order reaction rate constants for cresol destruction with each dye.

PROCESS PARAMETERS

HYDROGEN ION CONCENTRATION

For all tests run in buffered solutions pH varied by less than two-tenths of a pH unit during each experiment regardless of buffer used and buffer capacity. In the unbuffered test of 50 mg/l cresol

TABLE VII

AEROBIC PHOTO-OXIDATION RATE FOR 50 mg/l CRESOL WITH VARIOUS SENSITIZERS

Sensitizer (5 mg/l)	Reaction Rate ($-k$ min^{-1})	Half-life (min)
Methylene blue	0.283	2.45
Rose Bengal	0.253	2.74
2,7-dichlorofluorescein	0.005	138.6
Malachite green	0.038	18.23
Hematoporphyrin-D,L-hydrochloride	0.193	3.59
Acridine orange	0.027	25.7

with 5 mg/l methylene blue pH dropped from 7.8 to 7.2 in ten minutes of illumination.

Optimum pH and Buffer Dependence

The rate of dye sensitized aerobic photo-oxidation of cresol increases with increasing pH. Figure 8 is a plot of pH versus reaction rate for aerobic photo-oxidation of 50 mg/l cresol sensitized by 5 mg/l methylene blue.

The data in Figure 8 suggest two separate curves. The upper curve fits data from experiments in which Trizma (tris-(hydroxymethyl)

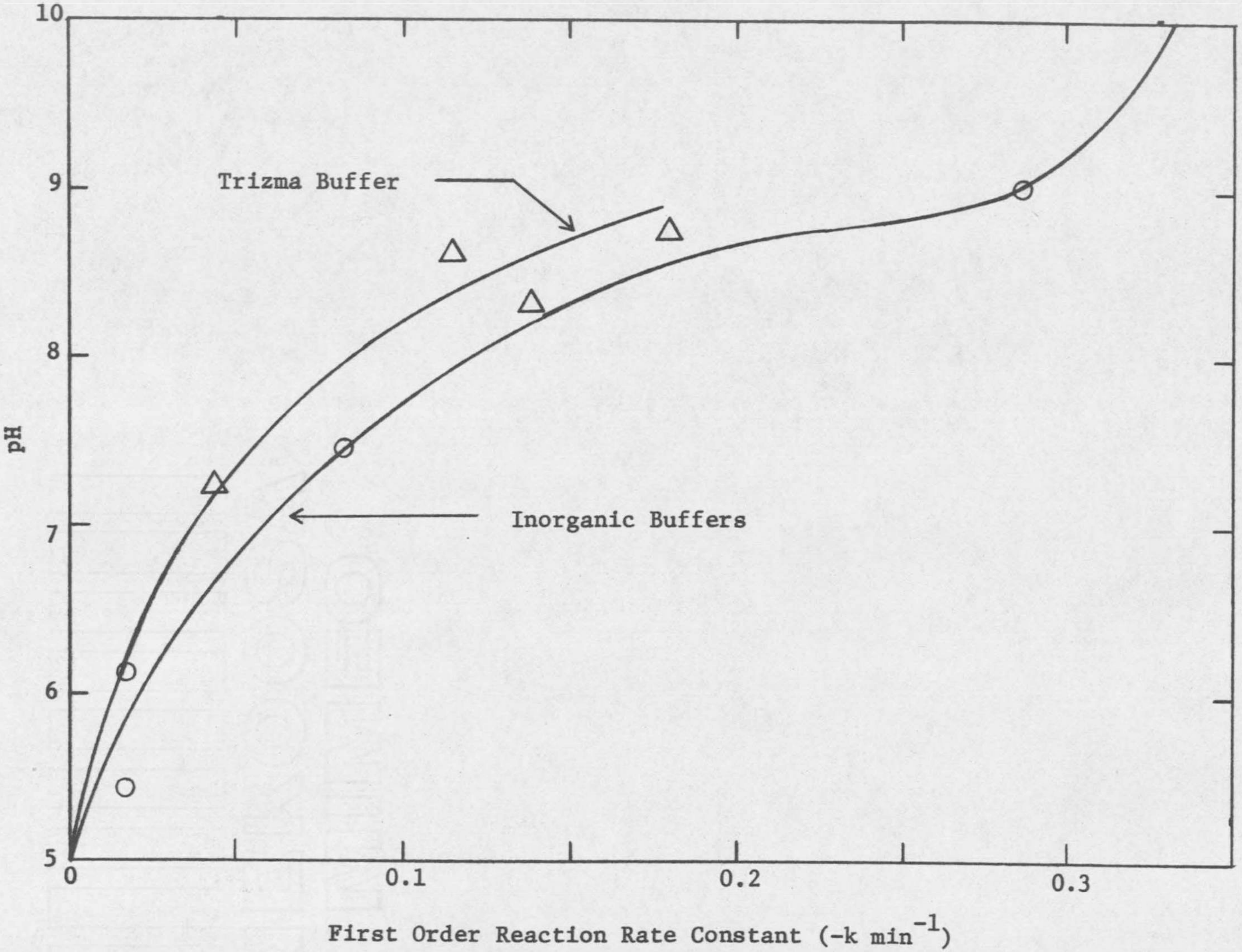


Fig. 8. REACTION RATE vs pH (50 mg/l INITIAL CRESOL, 5 mg/l METHYLENE BLUE)

aminomethane) titrated with HCl was the buffer system. The lower curve fits data from tests using the various other buffer materials.

Base Dependence

The rate of methylene blue sensitized aerobic photo-oxidation of cresol did not vary with buffer capacity of $NaHCO_3$ plus NaOH near pH 9. Figure 9 shows the slight variation of reaction rate with buffer capacity.

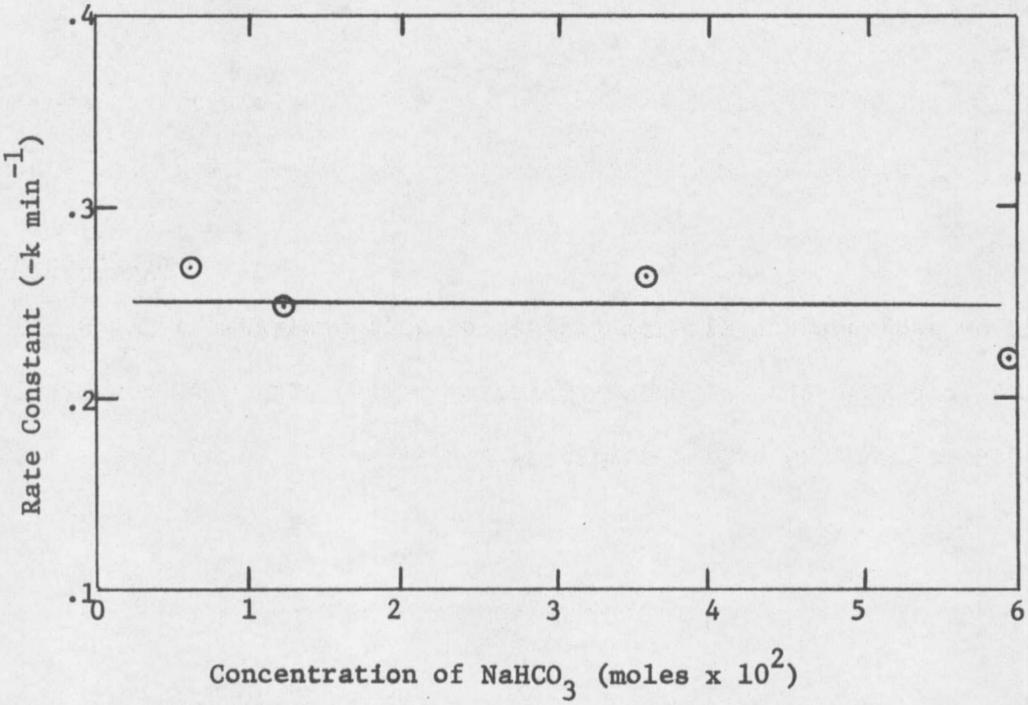


Fig. 9. REACTION RATE vs BUFFER CAPACITY WITH BUFFER SYSTEM $NaHCO_3$ PLUS NaOH IN 11.9 to 1 MOLAR RATIO (50 mg/l INITIAL CRESOL, 5 mg/l METHYLENE BLUE)

SENSITIZER CONCENTRATION

There is an optimum concentration of dye to sensitize aerobic photo-oxidation. The variation of reaction rate with sensitizer concentration is shown in Figure 10. The optimum methylene blue concentration to sensitize aerobic photo-oxidation of 50 mg/l cresol is about 5 mg/l. Sargent (1971) concluded optimum dye concentration is independent of substrate concentration.

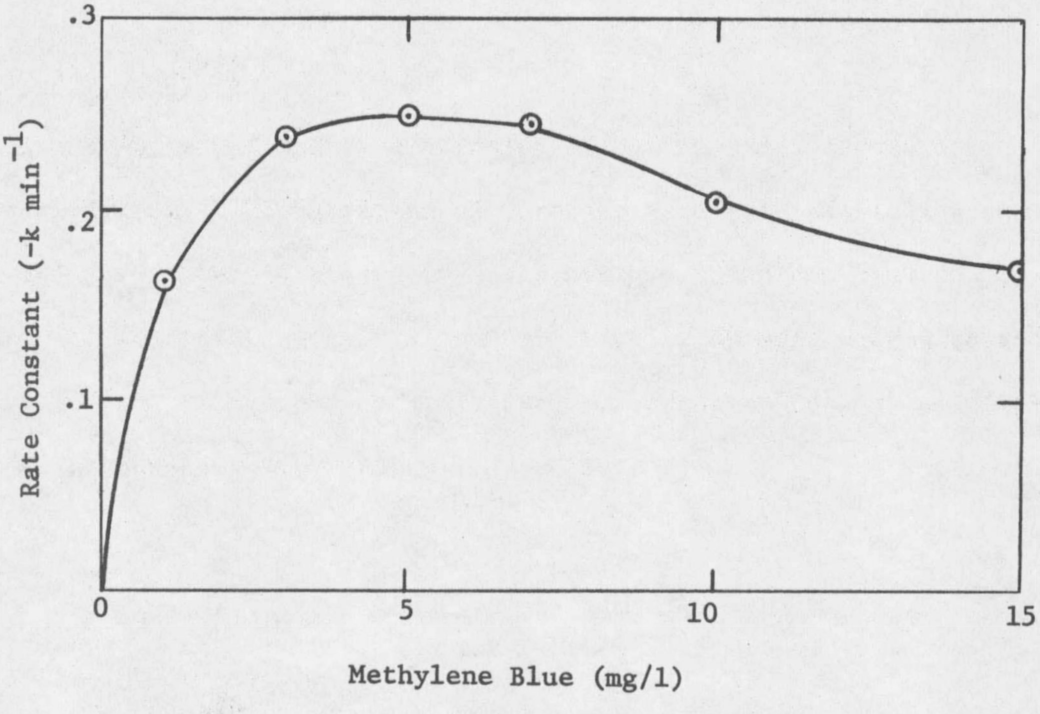


Fig. 10. REACTION RATE vs SENSITIZER CONCENTRATION (50 mg/l INITIAL CRESOL)

SUBSTRATE CONCENTRATION

Figure 11 shows how the rate of aerobic photo-oxidation of cresol sensitized by 5 mg/l methylene blue varies with initial cresol concentration. Initial cresol concentration is the amount of cresol in solution before photo-oxidation begins. There is an optimum initial cresol concentration and it is about 50 mg/l.

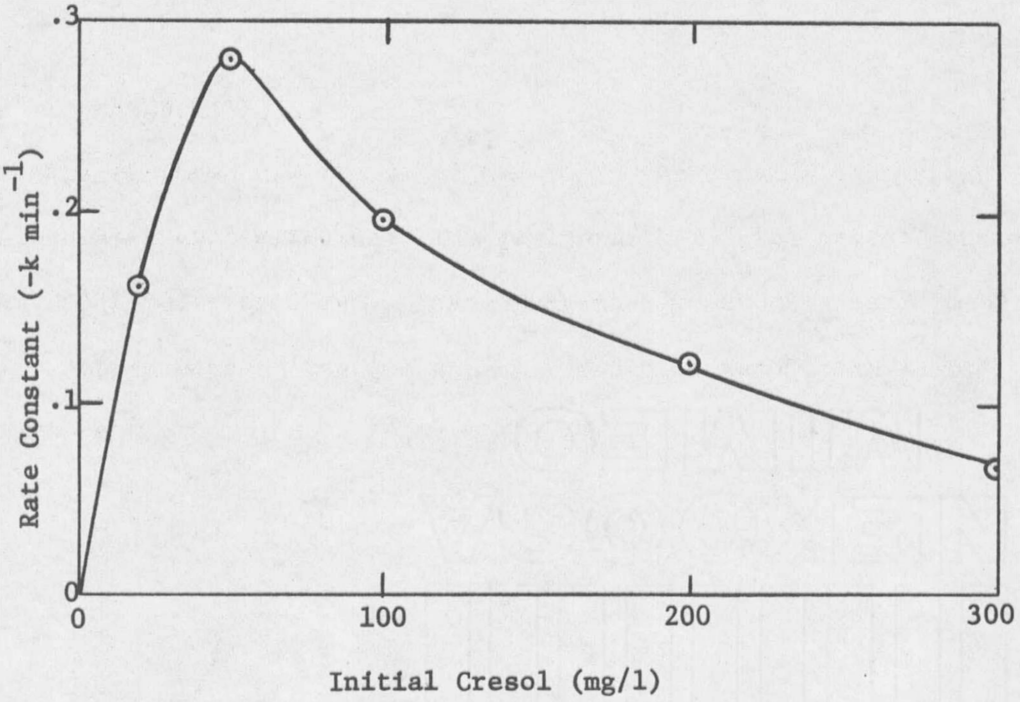


Fig. 11. REACTION RATE vs INITIAL CRESOL CONCENTRATION (5 mg/l METHYLENE BLUE)

LIQUID LAYER THICKNESS

In dye sensitized aerobic photo-oxidation, the reaction rate varies with thickness of the liquid layer upon which energizing light impinges. Figure 12 shows how the rate of aerobic photo-oxidation of cresol sensitized by methylene blue varies with thickness of the layer of reaction solution.

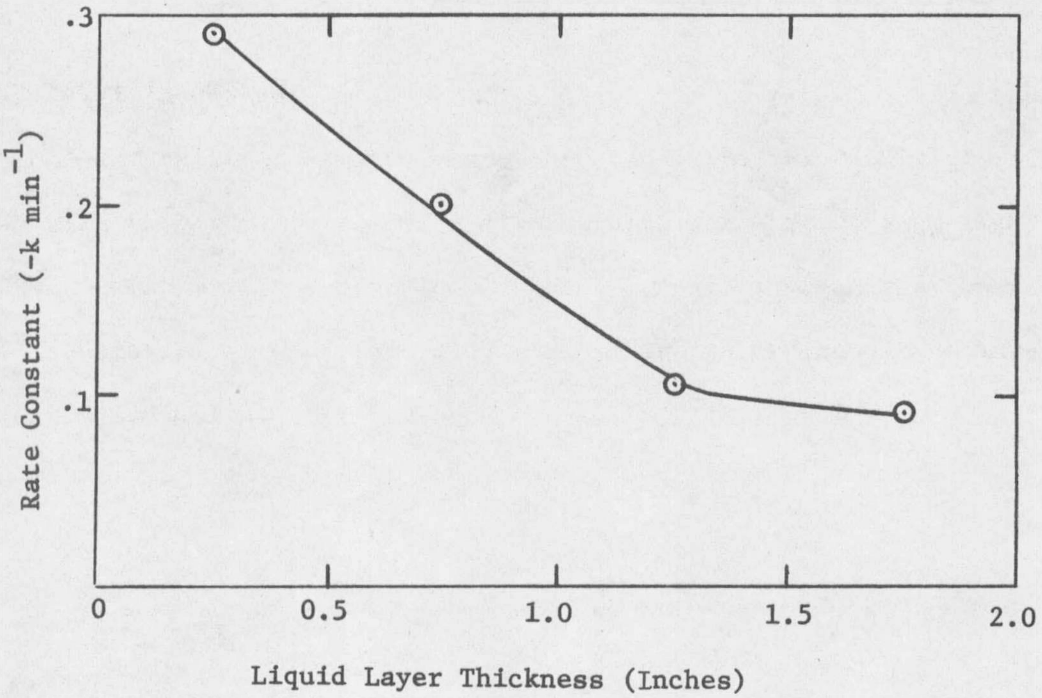


Fig. 12. REACTION RATE vs LIQUID LAYER THICKNESS
(100 mg/l INITIAL CRESOL, 5 mg/l METHYLENE BLUE)

LIGHT INTENSITY

The rate of dye sensitized aerobic photo-oxidation increases with increasing intensity of energizing light when the light source has the emission spectrum of Figure 6. The reaction rate increases with light intensity up to at least the spectral intensity shown in Figure 6. Figure 13 shows how the rate of aerobic photo-oxidation of cresol sensitized by methylene blue varies with light intensity.

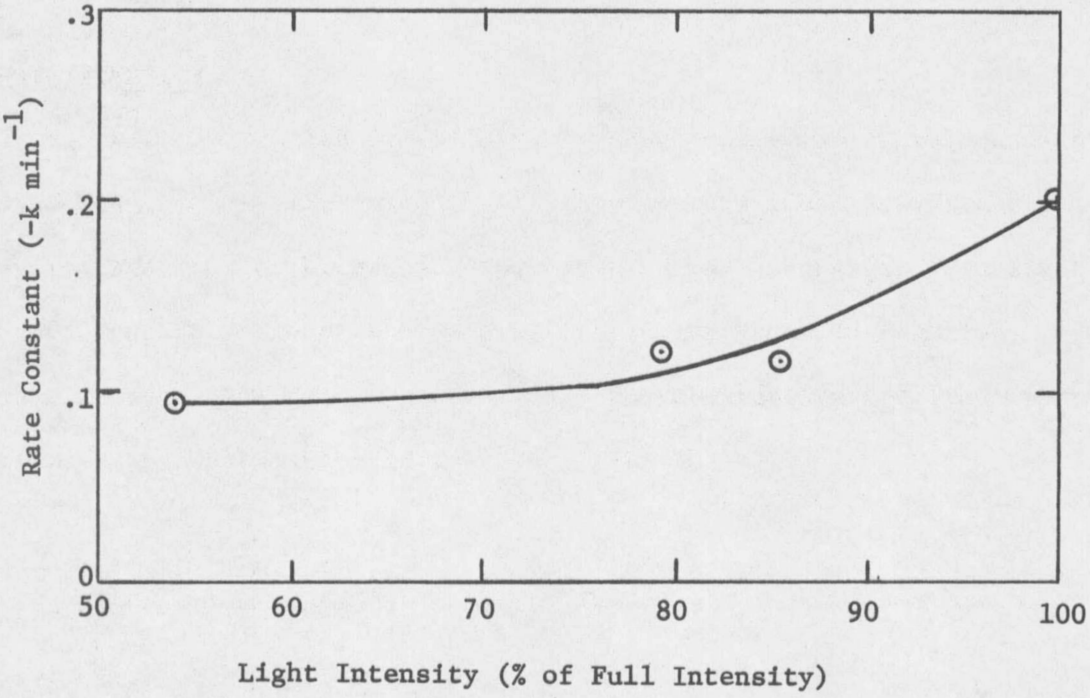


Fig. 13. REACTION RATE vs LIGHT INTENSITY
(100 mg/l INITIAL CRESOL, 5 mg/l
METHYLENE BLUE)

DYE PHOTO-REDUCTION

Methylene blue at 5 mg/1 is not measurably photo-reduced while sensitizing aerobic photo-oxidation of 100 mg/1 cresol when the energizing light has the emission spectrum shown in Figure 6. The first-order reaction rate constant for ten minutes of uninterrupted illumination is -0.196 min^{-1}. For ten minutes total illumination with one minute periods of light separated by one minute periods of no light the rate constant is -0.193 min^{-1}.

FLOW-THROUGH REACTION

The rate of aerobic photo-oxidation of 100 mg/1 cresol sensitized by 5 mg/1 methylene blue in flow-through process does not vary appreciably with detention time in the reactor. As detention time increases the first-order reaction rate constant varies neither systematically nor beyond experimental error. Because the reaction rate does not vary, cresol concentration in the effluent decreases exponentially as detention time increases. Changes in effluent cresol concentration and reaction rate constant with detention time are listed in Table VIII.

TABLE VIII

VARIATION OF EFFLUENT CRESOL CONCENTRATION AND RATE CONSTANT WITH DETENTION TIME

Detention Time (min)	Effluent Cresol Concentration (mg/l)	Rate Constant ($-k$ min^{-1})
3.6	58	0.152
4.7	42	0.185
7.0	30	0.172

RESIN-BOUND DYE

DYE BINDING

Duolite C-20X4 resin was coated with dye in methylene blue solutions of varying strengths to vary the amount of dye bound to resin. The amount of dye bound to resin is the difference between dye concentration before adding resin and dye concentration remaining in solution after the resin has been coated and removed. Table IX shows the various amounts of methylene blue remaining in solution after resin coating and the weight of dye on each 100 ml volume of wet resin.

REACTION RATE

Aerobic photo-oxidation of 100 mg/l cresol can be sensitized by methylene blue when the dye is attached to ion exchange resin. For

TABLE IX

METHYLENE BLUE BOUND TO DUOLITE C-20X4 RESIN

Dye Concentration Before Binding (mg/l)	Dye Concentration After Binding (mg/l)	Dye (mg) per 100 ml Resin
20	0	4.0
150	0.1	30.0
350	0.2	70.0
500	0.8	99.8
5000	1.6	999.7

resins tested in this study the reaction rate with bound dye is much less than the rate with dye dispersed in solution. In Table X are listed first order reaction rate constants for cresol destruction achieved with each resin when coated with methylene blue in 6 mg/l dye solution.

The rate of aerobic photo-oxidation sensitized by resin-bound dye varies erratically with amount of dye bound to resin for the conditions of this investigation. Figure 14 shows how the first-order reaction rate constant for cresol destruction varies with amount of dye bound to resin.

TABLE X

RATE CONSTANTS WITH RESIN BOUND DYE

Resin	Rate Constant ($-k$ min^{-1})
Duolite C-20X4	0.008
Dowex HCR	0.035
Duolite ES-80	0.038
Duolite C-25D	0.063
Powdex (PCH)	0.005

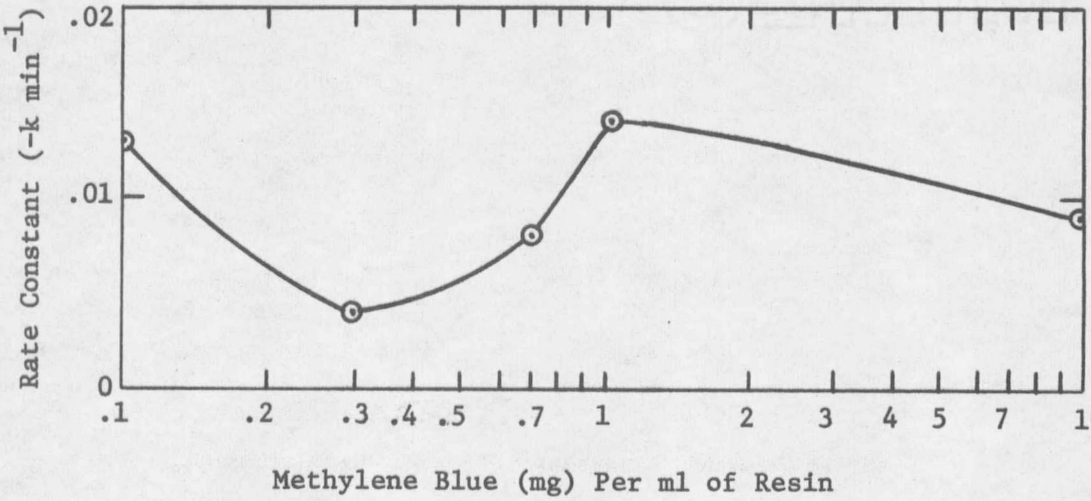


Fig. 14. REACTION RATE vs QUANTITY OF DYE ON RESIN (100 mg/1 INITIAL CRESOL, 5 mg/1 METHYLENE BLUE)

DYE BLEACHING

None of the dyes tested in this study were measurably bleached during any experiment with dye in dispersed solution. Bleaching is loss of color by dye.

Dye bound to resin was not tested for bleaching.

REACTIONS WITHOUT SINGLET OXYGEN

When light, oxygen, or sensitizer dye is eliminated from the methylene blue sensitized aerobic photo-oxidation system little cresol destruction is achieved. With the reaction solution swept by nitrogen to make it anaerobic, cresol concentration decreased only from 50 to 46 mg/l after ten minutes of illumination. When a buffered solution of 50 mg/l cresol and 5 mg/l methylene blue was aerated in the reactor with no light, cresol concentration decreased from 50 to 48 mg/l in ten minutes. No measurable cresol destruction occurred when 50 mg/l cresol was illuminated in the reactor without sensitizer dye for ten minutes.

In cresol solutions illuminated with resins lacking dye, no cresol was removed by ion exchange or adsorption on resin.

TEMPERATURE

The temperature of reaction solution did not change measurably during any of the experiments in this study. All tests were carried out at ambient room temperature (22.5° ± 2°C).

MIXING

The mixing characteristics of the flow-through reactor used in this study are described by the variation of rhodamine B dye concentration in reactor effluent with time after adding a dye slug at the inlet. The total mixed concentration of rhodamine B (the concentration which would obtain if the dye slug were completely dispersed in 800 ml of solution) is .0782 mg/l. Curve A in Figure 15 is a plot of the concentration of rhodamine B at the reactor outlet versus time. Time zero is when the dye slug was added at the reactor inlet.

OXYGEN TRANSFER

The rate of decrease in the dissolved oxygen deficit in 800 ml of distilled water aerated in the reactor of Figure 3 is shown in Figure 16. The slope of the curve in Figure 16 is defined as the first-order reaction rate constant for oxygen transfer, or the oxygenation coefficient. The oxygenation coefficient for the reactor is 0.59 min^{-1}.

RESULTS OF INDIVIDUAL TESTS

The first-order reaction rate constants for substrate destruction for all experiments performed in this study are listed in the Appendix beginning on page 95.

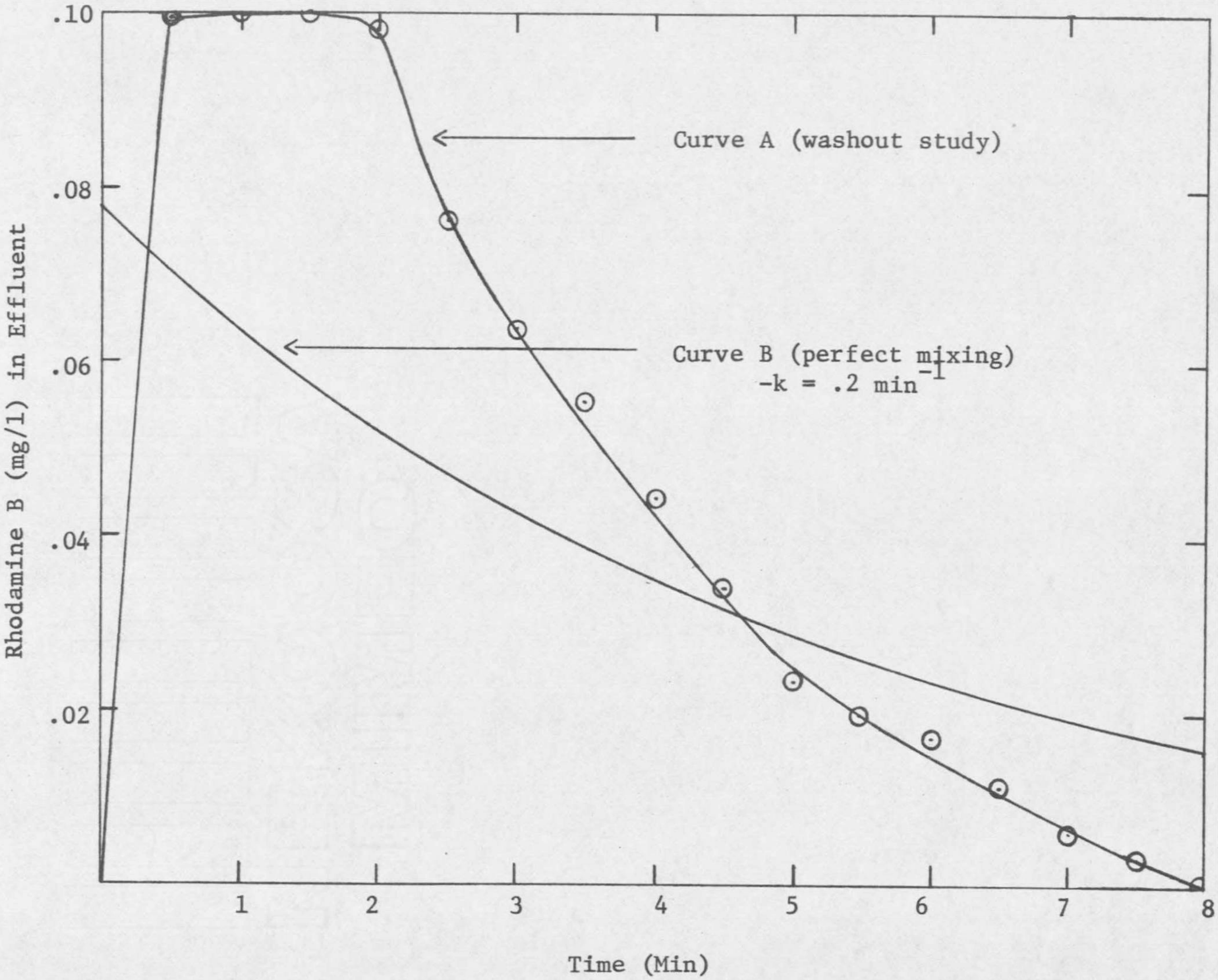


Fig. 15. COMPARISON OF MIXING IN REACTOR WITH PERFECT MIXING

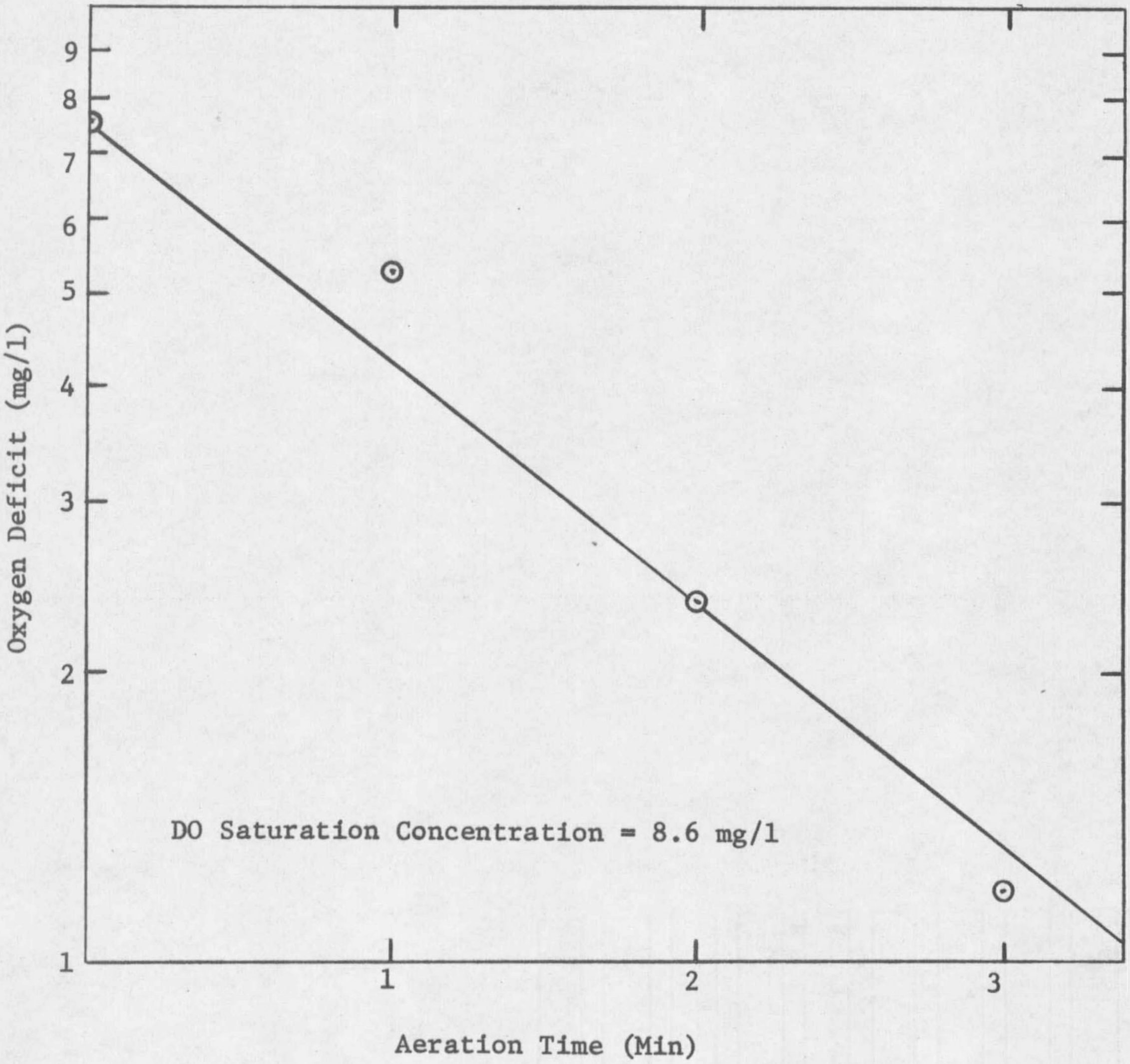


Fig. 16. DISSOLVED OXYGEN vs AERATION TIME
(DO = 8.6 - OXYGEN DEFICIT)

CHAPTER VI

DISCUSSION

REACTOR

PHYSICAL FEATURES

The reactor used in this study was designed to employ conventional engineering methods of aeration, mixing, and handling of waste streams. Mixing and oxygen transfer in the reactor are accomplished by diffuser aeration, a widely used engineering process. The reaction solution container is not of any special reflective or other shape requiring exotic fabrication.

The cast acrylic tubing used for the inner and outer walls and the water jacket transmits 92 percent of visible light according to commercial suppliers of the material. The plastic scratches easily and yellows slightly with age but during the two years of this study no measurable decrease in transmittance by the reactor walls was observed.

The purpose of the cooling fan shown in Figures 3 and 4 was to cool the lamps and extend their lifetimes.

LIGHT SOURCE

Fluorescent lamps were tested as sources of energizing light for dye sensitized aerobic photo-oxidation because they are more efficient than incandescent lamps and give off less heat. The negligible amount of photo-oxidation achieved with fluorescent lamps is probably caused by the low light intensity (see Figure 5).

With tungsten incandescent lamps light intensity in the reactor is about seventeen times the intensity from fluorescent lamps at the wavelength of peak absorption for methylene blue (see Figures 5 and 6). During experiments using incandescent lamps a water jacket is required between the lamps and reaction solution to absorb ultraviolet light and heat.

A feature of dye sensitized aerobic photo-oxidation giving it promise as a water or wastewater treatment method is its potential to be energized by direct sunlight. Light intensity in the reactor equipped with tungsten lamps is on the order of intensity of sunlight at the wavelength of peak absorption for methylene blue. Figure 17 is a comparison of an emission spectrum for sunlight with the emission spectrum from tungsten lamps in the reactor. The sunlight spectrum is from Iscotables (1970) and was measured February 21, 1966 at 11:30 A.M. at 40°49' N latitude and 96°42' W longitude (south-central Nebraska). The amount of sunlight available to energize a treatment process would vary with location, however, and depend on weather, the time of year, and other factors.

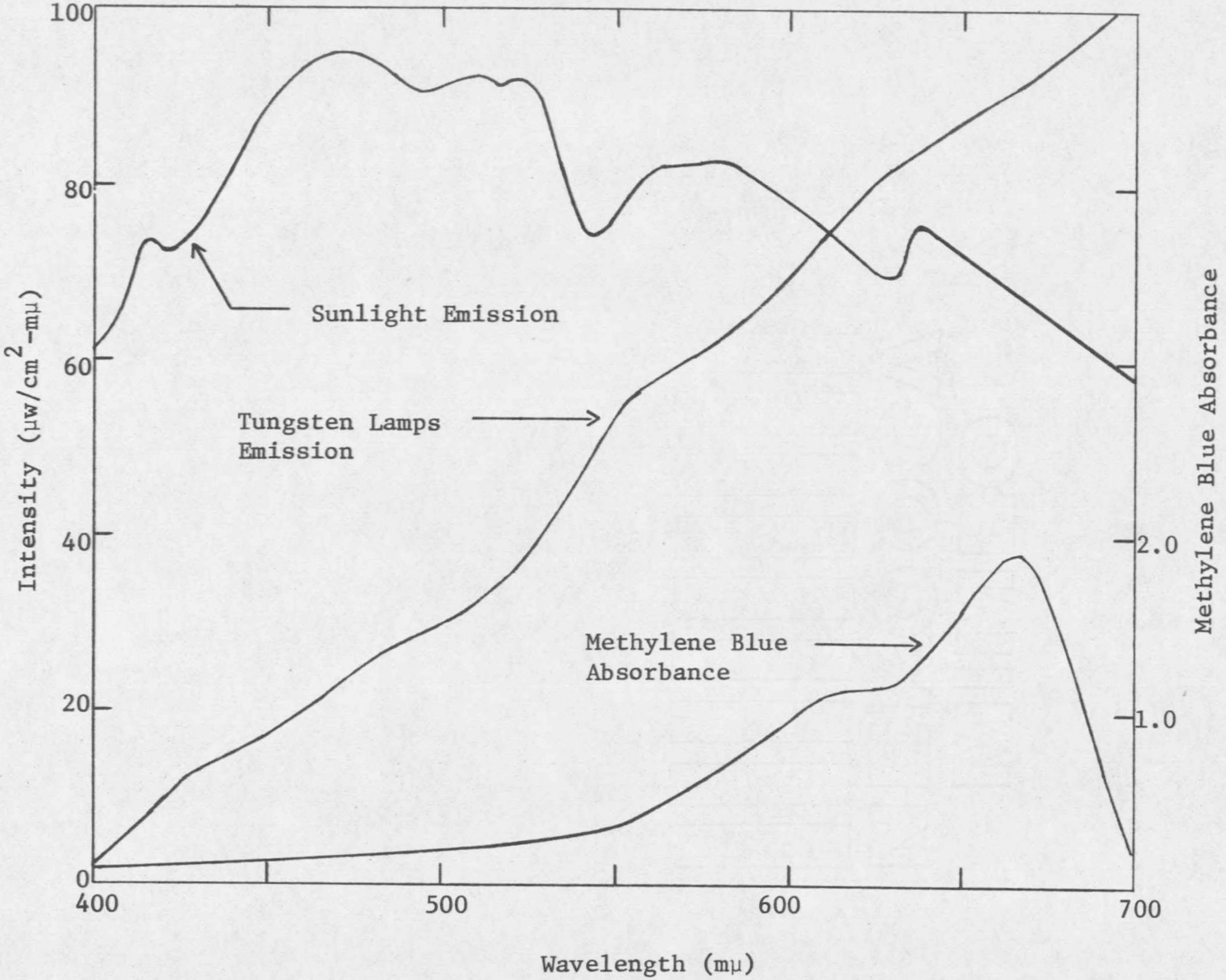


Fig. 17. COMPARISON OF SUNLIGHT WITH LIGHT IN REACTOR EQUIPPED WITH TUNGSTEN LAMPS

DYES

CHARACTERISTICS OF SENSITIZERS

The characteristics of a dye making it a good sensitizer for aerobic photo-oxidation are not well understood. However a few known factors are probably important. Certainly the dye must absorb some portion of the emission spectrum of energizing light, and presumably more is better. In addition the energy of the dye triplet must be at least 27 Kcal/mole if it is to energize formation of singlet oxygen. Foote (1968) indicates many dyes have triplet energies around 40 Kcal/mole. Having a relatively long-lived triplet state and high quantum yield for triplet formation are probably further requirements of a good sensitizer.

The electronic configuration of a dye is probably an important factor affecting efficiency of energy transfer from triplet sensitizer to oxygen or other molecules. If a specific juxtaposition of molecules is a prerequisite of energy transfer, a certain shape might be required of a dye for it to be compatible with oxygen in energy transfer. Also, the extent to which triplet dye and singlet oxygen are quenched by water or other materials in solution could be a function of electronic configuration.

TEST RESULTS

Of the dyes tested in this study, methylene blue and Rose Bengal are by far the most effective sensitizers of aerobic photo-oxidation of both cresol and phenol. Minimum half-life of cresol was 2.45 minutes with methylene blue and 2.74 minutes with Rose Bengal.

No aerobic photo-oxidation of either cresol or phenol was observed with Na-phthalocyanine, rhodamine 6G, and neutral red as sensitizers. Some phthalocyanine dyes have evinced long-lived triplet states and high quantum yields for triplet production, but the dye was insoluble enough under the conditions of this study to be ineffective as a sensitizer. Neutral red and rhodamine 6G have absorption peaks at wavelengths of relatively low emission from tungsten lamps, which perhaps explains in part their ineffectiveness as sensitizers.

Measurable destruction of cresol was sensitized by 2,7-dichlorofluorescein using both fluorescent and tungsten lamps. On the other hand no phenol destruction was observed with the same dye. This suggests certain dyes might be substrate specific with respect to effectiveness as sensitizers.

Malachite green and acridine orange were about equally able to sensitize relatively slow destruction of phenol and cresol. Cresol half-life with both dyes was about 22 minutes. It is curious that malachite green is a much less effective sensitizer than methylene blue and Rose Bengal considering its absorption peak is between the absorption peaks for the other two dyes.

Hematoporphyrin-D,L-hydrochloride was a fairly good sensitizer for cresol destruction. Cresol half-life was 3.6 minutes with this dye. Phenol half-life with the same dye was 15.4 minutes. Hence hematoporphyrin-D,L-hydrochloride is inexplicably a moderately good sensitizer for aerobic photo-oxidation.

There seems to be no firm theoretical basis for predicting how well a given dye will sensitize singlet oxygen formation. Furthermore, it is seldom possible to explain from theory why certain dyes are good sensitizers and others are not.

SUBSTRATE SPECIFICITY

Methylene blue and Rose Bengal sensitize cresol destruction about three times faster than they sensitize phenol destruction. With hematoporphyrine-D,L-hydrochloride, cresol destruction was about four times faster than phenol destruction. These differences in reaction rates with cresol and phenol might be expected since singlet oxygen is more reactive with cresol than with phenol. If substrate oxidation involves a free singlet oxygen mechanism, the rate of oxidation should depend only on singlet oxygen-substrate reactivity and not on dye-substrate interactions. The fact that the ratio of cresol destruction rate to phenol destruction rate for all three dyes was nearly the same is evidence for the free singlet mechanism.

2,7-dichlorofluorescein, on the other hand, gives evidence of being substrate specific. The dye will sensitize some cresol destruction but no phenol destruction. This might be evidence for other than a free singlet oxygen mechanism.

PROCESS PARAMETERS

HYDROGEN ION CONCENTRATION

Optimum pH

The results of this and many earlier studies show conclusively that high pH favors dye sensitized aerobic photo-oxidation. For one thing substrates with ionizable protons will be more completely ionized at high pH leaving greater electron density at the site of ionization. The increased electron density enhances reactivity with singlet oxygen. Figure 18 shows the correlation between cresol ionization and cresol destruction as pH increases. That correlation was previously demonstrated by Bellin and Yankus (1968) and others. Furthermore at high pH excess hydroxyl ions are available to take up any hydrogen ions which might be freed if singlet oxygen extracts electrons from substrate.

The rate of dye sensitized aerobic photo-oxidation increases with pH at least to pH 10. But since there are usually practical limits on pH adjustment in water and wastewater treatment, 9 to 10 might be the optimum pH range for the process.

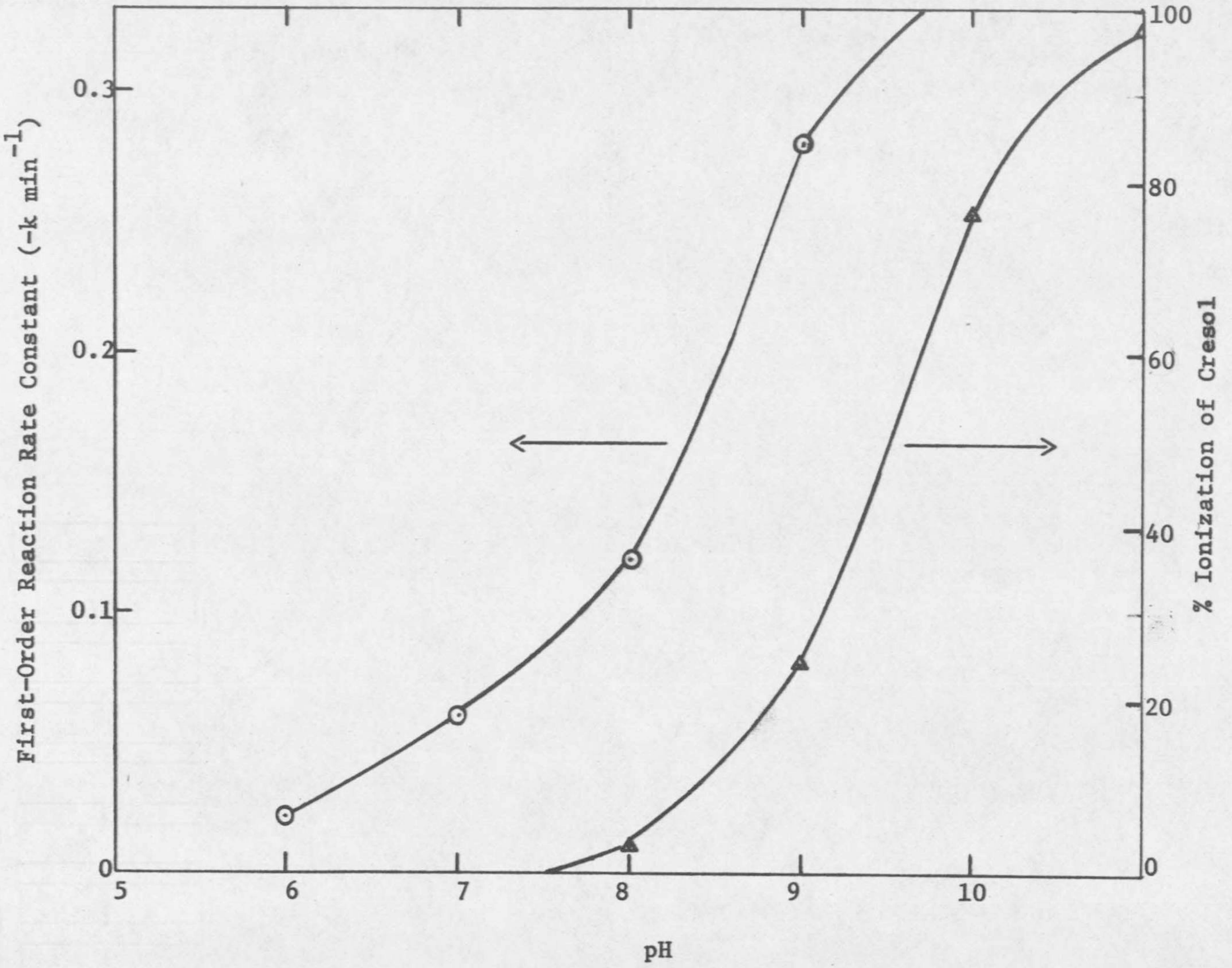


Fig. 18. COMPARISON OF CHANGES IN CRESOL DESTRUCTION RATE AND PERCENT IONIZATION OF CRESOL WITH pH (50 mg/l INITIAL CRESOL, 5 mg/l METHYLENE BLUE)

Buffer Dependence

Figure 8 shows the reaction rate constant for aerobic photo-oxidation of 50 mg/l cresol sensitized by 5 mg/l methylene blue can vary at a given pH depending on buffer used. The upper curve indicates reaction rate with a Trizma-HCl buffer system is slower than with the other buffers tested. Apparently Trizma, a relatively complex organic chemical, is involved in quenching or in secondary reactions which interfere with dye sensitized aerobic photo-oxidation. Trizma may also increase solution viscosity, thereby hindering interaction among dye, oxygen, and substrate.

Inorganic buffers exhibit less interference with reaction rate, and this is consistent with the findings of Bellin and Yankus (1968). They concluded inorganic ions interfere neither with dye sensitized singlet oxygen formation nor with singlet oxygen-substrate interaction.

Base Dependence

Figure 9 shows that aerobic photo-oxidation of cresol is not a general base dependent reaction since the reaction rate is independent of buffer capacity. This is further evidence that inorganic ions do not interfere with the process. It is also evidence that increasing the concentration of unionized inorganic molecules in solution does not inhibit the reaction.

SENSITIZER CONCENTRATION

According to Beer's law light absorbance by a substance in solution increases linearly with concentration of absorbent. Accordingly absorption of light energy by a sensitizer dye increases exponentially with dye concentration within the range of concentrations for which Beer's law holds. More light absorption by sensitizer means more triplet dye formation followed by singlet oxygen generation. Too much dye, however, can result in quenching of triplet dye by ground state dye and direct reaction between sensitizer and substrate.

The optimum sensitizer concentration for dye sensitized aerobic photo-oxidation probably varies depending on sensitizer used, substrate to be oxidized, liquid layer thickness, and other factors. For aerobic photo-oxidation of 50 mg/l cresol the optimum methylene blue concentration is about 5 mg/l for the reaction conditions used to optimize sensitizer concentration.

SUBSTRATE CONCENTRATION

Figure 11 indicates there is an optimum initial substrate concentration to obtain the maximum first-order reaction rate in methylene blue sensitized aerobic photo-oxidation of cresol. This means the process rate is not a first-order function of substrate concentration. Perhaps cresol oxidation products become involved in secondary reactions that effect the reaction rate. As cresol concentration increases from that optimum the first-order reaction rate constant decreases, but the total weight of cresol oxidized increases. Hence treatment objectives must be known before optimum substrate concentration can be determined.

From Figure 11, the optimum initial cresol concentration is about 50 mg/l. But the rate constant does not change rapidly with initial cresol concentration, especially as initial cresol concentration increases. An acceptable rate of dye sensitized aerobic photo-oxidation of substrate can probably be achieved over at least a 10^{-3} molar range of substrate concentration.

LIQUID LAYER THICKNESS

All dye molecules in the reactor of Figure 3 are not the same distance from the lamps. For thin liquid layers all dye molecules are near the outer wall of the reactor. As the liquid layer increases, however, the edge of the reaction solution away from the lamps moves farther from the lamps. Beer's law states the energy of light impinging on a light absorbing solution decreases exponentially as it passes through the solution. Hence the energy absorbed per molecule of absorbent decreases as thickness of the liquid layer increases. Furthermore, light energy must travel farther through reaction solution to reach all dye molecules in thicker liquid layers. This increases absorption and scattering of light by solvent and other molecules in solution. Accordingly, the quantum yield of energy absorption by sensitizer, and hence the rate of substrate oxidation should decrease with increasing liquid layer thickness.

Figure 12 shows how the reaction rate increases with decreasing liquid layer thickness to a liquid layer of at least 1/4 inch. But confining a waste stream in a very thin layer can make it difficult to pass the required fluid volume economically. For that reason, 3/4 inch was selected as optimum liquid layer thickness for this study.

LIGHT INTENSITY

An increase in light intensity impinging on a dye solution increases the amount of light energy available for absorption by dye molecules. More energy absorption would result in more triplet dye and singlet oxygen formation and a faster rate of aerobic photo-oxidation.

In this study reaction rate did increase with light intensity (see Figure 13). As light intensity increased in the reactor, energy transfer from sensitizer to oxygen increased and cresol was oxidized faster. There is probably a limit to the reaction rate attainable by increasing light intensity, but that limit was not reached in this study.

DYE PHOTO-REDUCTION

When a dye is photo-reduced it loses color, and bleached dye does not sensitize singlet oxygen formation. To preserve dye and maintain maximum sensitization rate, photo-reduction of sensitizer must be minimized.

In an earlier investigation Sargent (1971) observed bleaching of methylene blue during dye sensitized aerobic photo-oxidation of cresol. Light intensity in the reactor used in that study was much greater than intensities achieved in the reactor of Figure 3. Also, the reaction solution was not cooled. On the other hand no dye bleaching was observed during any experiments of the study herein reported. Apparently, the greater light intensity and heat caused dye destruction in the earlier tests.

Since no dye bleaching was observed in tests with continuous illumination, little increase in reaction rate should result from breaking the illumination period into periods of light interspersed with periods of no light. In this study the reaction rate with continuous illumination was about the same as the rate with periods of no light alternating with periods of light.

The resistance of methylene blue in well-designed reactors augurs well for the stability of the dye in a treatment process energized by sunlight.

REACTIONS WITHOUT SINGLET OXYGEN

Since sensitizer dye, oxygen, and light were essential ingredients to achieve substrate destruction in this study, substrate was destroyed by dye sensitized aerobic photo-oxidation. Mechanisms other than a free singlet oxygen mechanism are possible under these conditions, but the weight of evidence in the literature supports a free singlet mechanism. Cresol destruction in tests with resin-bound dye was also by dye-sensitized aerobic photo-oxidation.

FLOW-THROUGH REACTION

MIXING

In a perfectly mixed reactor a slug of soluble material added is immediately dispersed and diluted as a first-order function of the ratio of flow rate to reactor volume. Hence, the concentration of the material in the reactor effluent decreases exponentially and the rate constant is the ratio of flow rate (160 ml/min) to reactor volume (800 ml) or .2 min^{-1}.

The data from the washout study for the reactor of Figure 3 do not plot as a first order function. Figure 15 is a comparison of data from the washout study (curve A) with the theoretical curve the data would describe if the reactor were perfectly mixed (curve B). The plateau in curve A between times 30 seconds and 90 seconds suggests a plug flow regime, but the tailing off of the curve after 90 seconds is characteristic of perfect mixing. Therefore, the mixing characteristics of the reactor lie between plug flow and perfect mixing.

Levenspiel (1962) describes a parameter called the reactor dispersion number used to indicate the extent to which a reactor is completely mixed. The reactor dispersion number varies from zero for plug flow to infinity for perfect mixing. According to Levenspiel a reaction dispersion number of 0.002 represents a small amount of mixing, 0.025 indicates intermediate dispersion by mixing, and 0.2 means the reactor is well mixed. The reactor dispersion number for the reactor used in this study is 0.29, indicating it is well mixed.

REACTION RATE

If the reactor used in this study were a plug flow reactor the rate of dye sensitized aerobic photo-oxidation observed in flow-through reaction should be the same as the batch test rate for a given set of reaction conditions. For example, if cresol is reduced from 100 mg/1 to 50 mg/1 by methylene blue sensitized aerobic photo-oxidation after three minutes of illumination in batch reaction, the same reduction in cresol should be obtained in plug flow reaction with a detention time of three minutes.

In a perfectly mixed reactor the reaction rate is less than that obtained in batch tests for a given set of reaction conditions. A mass balance on a perfectly mixed reactor can be written as:

$$C_oQ = C_eQ + kVC_e \qquad (4)$$

where C_o is substrate concentration flowing into the reactor, C_e is effluent substrate concentration, Q is flow rate, V is reactor volume and k is the first-order rate constant for destruction of substrate in the reactor. Dividing all terms by Q gives:

$$C_o = C_e + ktC_e \qquad (5)$$

where t is detention time (V/Q) or illumination time. Rearranging equation (5) yields:

$$C_e = C_o/(1+kt) \qquad (6)$$

Using equation (6) to calculate effluent concentration for various detention times shows C_e is greater in the effluent of a perfectly mixed reactor than in the effluent of a plug flow reactor for a given reaction rate constant (k) and detention time (t).

In Figure 19 the rates of cresol destruction actually achieved in flow-through tests (curve A) are compared with theoretical rates which would be observed in plug flow (curve B) and perfectly mixed (curve C) reactors. The data from actual tests (curve A) fall between curves B and C confirming the washout study results that mixing characteristics of the reactor are between plug flow and perfect mixing.

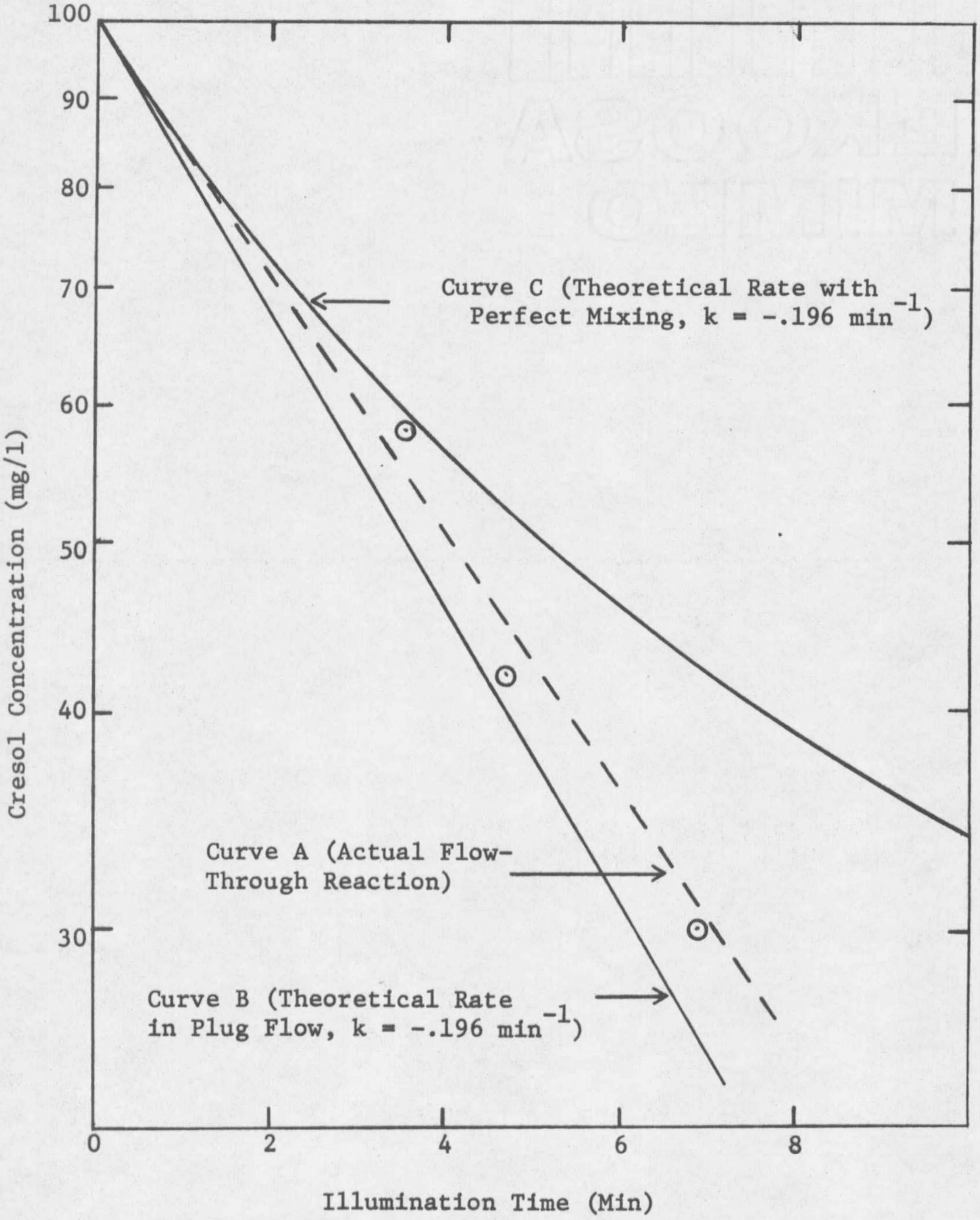


Fig. 19. COMPARISON OF FLOW-THROUGH REACTION RATE WITH THEORETICAL RATES IN PLUG FLOW AND PERFECTLY MIXED REACTORS (100 mg/1 INITIAL CRESOL, 5 mg/1 METHYLENE BLUE)

RESIN-BOUND DYE

Binding methylene blue to ion exchange resins reduces its effectiveness as a sensitizer for aerobic photo-oxidation of cresol. Bellin and Yankus (1968) also observed loss of sensitizing ability for polymer-bound dyes but could only speculate on why it occurred.

The first order rate constants for cresol destruction with methylene blue bound to Dowex HCR, Duolite C-25D, and Duolite ES-80 resins are between -0.0348 and -0.0501 min^{-1} (see Table X). Why the reaction rates with those three resins should be nearly the same, but four times the rate with Duolite C-20X4, is not readily apparent from the physical characteristics of the resins. Dowex HCR is a copolymer of styrene, 8 percent cross-linked with divinyl benzene (DVB), and with sulfonate functional groups. Duolite C-25D is also a sulfonated copolymer of styrene and DBV but with 5.5 percent cross-linking. Duolite ES-80, on the other hand, is an acrylic polymer with carboxylate functional groups and cross-linked with an aromatic polymer similar to DVB. Duolite C-20X4 is a sulfonated copolymer of styrene and DVB similar to C-25D and HCR.

With methylene blue bound to Powdex resin the first order rate constant for cresol destruction was only -0.0047 min^{-1}. Powdex is a strong acid cation exchanger which has been ground into very small particles (see Table III). For some reason attaching the dye to the very small particles of resin greatly inhibits its sensitizing ability.

Bradley and Wolf (1959) concluded the absorption spectrum of a dye bound to a polymer could be changed by varying the ratio of dye to polymer. Accordingly the sensitizing ability of a bound dye might be a function of the dye to polymer ratio. But Figure 14 shows no systematic variation in cresol destruction rate with Duolite C-20X4 resin coated with varying amounts of dye (see Table IX). In this study the influence of the dye to polymer ratio on cresol destruction rate may be overshadowed by some other factor limiting the process.

It is significant that resin-bound dye did prove capable of sensitizing singlet oxygen formation, albeit at a slower rate than dispersed dye. The degree to which dye binding inhibits the reaction rate probably varies for different polymers and dyes. The method by which dye is attached to a polymer is also probably important. Further experimentation with different dyes and polymers and methods of linking them might lead to a combination which leaves the dye free to sensitize singlet oxygen formation nearly as efficiently as dispersed dye.

OXYGEN TRANSFER

The oxygenation coefficient or first-order rate constant for oxygen transfer in the reactor of Figure 3 is 0.59 min^{-1}. Saturation concentration for dissolved oxygen is 8.6 mg/l at the temperature and pressure of this study. Since the rate of singlet oxygen generation is independent of dissolved oxygen concentration down to trace amounts of dissolved oxygen, singlet oxygen formation is limited by oxygen transfer only when dissolved oxygen concentration approaches zero. Also, the maximum quantity of oxygen in terms of moles per liter will be transferred to reaction solution when dissolved oxygen concentration approaches zero. Assuming it is desirable to maintain at least 1 mg/l dissolved oxygen, maximum oxygen deficit is 8.6 minus 1 or 7.6 mg/l (4.75×10^{-4} M). At that deficit, the oxygen transfer rate in the reactor is (4.75×10^{-4}) times 0.59 or 0.285×10^{-3} moles per minute.

The maximum rate of cresol disappearance in terms of moles per liter can be calculated for a given experiment using the first-order rate constant and initial cresol concentration. Table XI lists the maximum rates of cresol destruction in moles per liter for the various different initial cresol concentrations.

TABLE XI

CRESOL DESTRUCTION RATES IN MOLES PER LITER

Initial Cresol (moles/liter)	Rate Constant ($-k$ min^{-1})	Destruction Rate (moles/min)
$2.78\text{x}10^{-3}$	0.065	$1.8\text{x}10^{-4}$
$1.85\text{x}10^{-3}$	0.121	$2.2\text{x}10^{-4}$
$9.30\text{x}10^{-4}$	0.196	$1.8\text{x}10^{-4}$
$4.60\text{x}10^{-4}$	0.283	$1.3\text{x}10^{-4}$
$1.90\text{x}10^{-4}$	0.160	$3.0\text{x}10^{-5}$

From Table XI the maximum rate of cresol destruction is 2.2×10^{-4} moles/min. Since oxygen can be transferred at 2.85×10^{-4} moles/min, oxygen transfer was not limiting in this study if the destruction of one mole of cresol consumes one mole of oxygen. Figure 2 shows that the opening of cresol's aromatic ring probably consumes only one molecule of oxygen per molecule of cresol. Further oxidation by singlet oxygen of the products of ring opening is possible. But singlet oxygen is very reactive with the sites of high electron density in ionized cresol. Hence the reaction of one molecule of singlet oxygen with one molecule of cresol to open the aromatic ring probably predominates until the cresol concentration becomes low. This analysis is conservative in that it does not consider oxygen available in solution before photo-oxidation begins.

DATA ANALYSIS

For ninety percent of the experiments performed the data did not deviate from the fitted first-order curve by more than ten percent. In no experiment did the data deviate by more than 20 percent from the fitted curve.

The data from each experiment were fitted to the first-order kinetics equation $C = C_o e^{kt}$ for convenience in expressing experimental results. This is not meant to imply the mechanism of dye sensitized aerobic photo-oxidation is simply a first-order function of substrate concentration. This investigation and many others have shown the process rate to be a function of at least sensitizer concentration, light intensity, pH, and electronic properties of sensitizer and substrate.

ECONOMICS

Cost is a critical consideration in developing any water or wastewater treatment process. However, it is difficult to generalize on the cost of dye sensitized aerobic photo-oxidation for several reasons, including: (1) a method of dye application and recovery has yet to be developed, (2) the physical features and hence cost of a plant to house the process are not known, and (3) rate of waste oxidation will vary greatly depending on such things as chemical properties of waste molecules, pH adjustment required, oxygen requirement, sensitizer used, and degree of treatment required.

An important economic advantage of dye sensitized aerobic photo-oxidation is its potential to use direct sunlight as an energy source. If electrically powered lamps must be used the process will suffer the same cost drawbacks as treatment methods using ultraviolet light.

Sensitizer dyes are relatively expensive as waste treatment chemicals, but on the other hand only low concentrations are required. A possible method of dye application is in dispersed solution to achieve singlet oxygen formation, followed by removal of dissolved dye by ion exchange. Strong and weak acid cation exchange resins are very selective for most cationic dyes so dye removal is complete, but regeneration of the resin after dye removal would probably prove impractical. Hence disposal of dye saturated resin would be necessary.

One bed volume of Duolite C-20X4 resin proved capable in this study of removing 5 mg/l of methylene blue from about 50,000 bed volumes of solution. At a resin cost of $26.00 per cubic foot, the purchase price of resin to remove dye from solution would be about seven cents per thousand gallons. One thousand gallons of a 5 mg/l methylene blue solution contains 0.0416 pounds of dye. At a dye cost of $1.00 per pound it would cost about four cents per thousand gallons of waste stream to supply dye. The combined purchase price for dye and resin to be used once and discarded would be eleven cents per thousand gallons. Of course if a method of dye recyle could be developed, dye and resin costs would be greatly reduced.

Capital cost, power cost for aeration and waste stream handling, final costs of materials, and operation and maintenance costs for a particular application will depend on such things as physical plant requirements, strength and content of waste stream, oxygen requirement, degree of treatment required, and method of dye application used. A definitive economic analysis of dye sensitized aerobic photo-oxidation applied to waste treatment awaits development of a dye application and recovery method, testing the process with sunlight, and experimentation with actual waste streams.

CHAPTER VII

CONCLUSIONS

Photo-chemical reactions can be very complex. Many different mechanisms are possible depending on a multitude of reaction conditions. Accordingly conclusions based on the results of testing a particular photo-chemical process do not necessarily apply to all or even any other photo-chemical processes. Conclusions drawn from the results of this study are separated into two categories: (1) those which apply to dye sensitized aerobic photo-oxidation in general, and (2) those which are true only for the particular conditions under which dye sensitized aerobic photo-oxidation was tested in this study.

GENERAL CONCLUSIONS

1. Dye sensitized aerobic photo-oxidation can be achieved in a process employing conventional engineering methods of aeration, mixing, and handling of waste streams.
2. Cresol and phenol can be destroyed by dye sensitized aerobic photo-oxidation. Cresol is destroyed faster than phenol.
3. The reaction of singlet oxygen with aromatic heterocyclic compounds which are refractory to conventional waste treatment processes probably gives products tractable to

biological oxidation. The reaction products were not tested for biodegradability.

4. High pH (9 to 10) favors dye sensitized aerobic photo-oxidation. The reaction rate can depend on the type of buffer system used to maintain desired pH.
5. Dye sensitized aerobic photo-oxidation is not general base dependent with inorganic buffer systems.
6. The rate of dye sensitized aerobic photo-oxidation increases with light intensity and decreases with thickness of the liquid layer of reaction solution.
7. Dye bound to ion exchange resin can sensitize aerobic photo-oxidation of substrate.
8. Dye sensitized aerobic photo-oxidation has potential as a waste treatment method. Further study is necessary to develop a dye application and recovery method and to test the process with sunlight and actual waste streams.

FOR CONDITIONS OF THIS STUDY

1. The rate of substrate destruction by dye sensitized aerobic photo-oxidation can be accurately described by the first-order kinetics equation $C = C_o e^{kt}$.
2. Optimum dye concentration to achieve aerobic photo-oxidation of 50 mg/l cresol is about 5 mg/l.

3. Optimum initial cresol concentration for maximum rate of aerobic photo-oxidation sensitized by 5 mg/l methylene blue is about 50 mg/l. Minimum cresol half-life is 2.45 minutes.
4. Commercially available fluorescent lamps are ineffective as energizers for dye sensitized aerobic photo-oxidation.
5. Dye sensitized aerobic photo-oxidation can be achieved with tungsten incandescent lamps as light source.
6. Methylene blue and Rose Bengal are effective sensitizers. Hematoporphyrin-D,L-hydrochloride is a moderately good sensitizer; but Na-phthalocyanine, rhodamine 6G, neutral red, malachite green, 2,7-dichlorofluorescein, and acridine orange are ineffective as sensitizers for dye sensitized aerobic photo-oxidation.
7. The rate of dye sensitized aerobic photo-oxidation increases with decreasing liquid layer thickness of reaction solution. Significant substrate destruction can be achieved with liquid layer thickness of almost two inches.
8. Attaching methylene blue to ion exchange resin decreases its ability to sensitize aerobic photo-oxidation of cresol by as much as 95 percent. The reaction rate with resin bound dye is independent of the dye to polymer ratio.

APPENDIX

RESULTS OF ALL TESTS

With fluorescent lamps, 50 mg/l initial cresol, 3/4 inch liquid layer thickness, and pH 9 buffered with Trizma and HCl:

Dye	Dye Conc. (mg/l)	$-k(\text{min}^{-1})$
Methylene Blue	1	0.011
Methylene Blue	5	0.016
Methylene Blue	10	0.014
2,7-Dichlorofluorescein	5	0.003
2,7-Dichlorofluorescein	10	0.004
Na-Phthalocyanine	50 (approx.)	0.000
Rhodamine 6G	5	0.000
Neutral Red	saturated	0.000

All Remaining Tests With Tungsten Lamps

With 50 mg/l initial cresol, 3/4 inch liquid layer thickness, and pH 9 buffered with $NaHCO_3$ and NaOH:

Dye	Dye Conc. (mg/l)	$-k(\text{min}^{-1})$
Methylene Blue	5	0.283
Rose Bengal	5	0.253

2,7-Dichlorofluorescein	5	0.005
Malachite Green	5	0.038
Hematoporphyrin-D,L-hydrochloride	5	0.193
Acridine Orange	5	0.027

With 50 mg/1 initial phenol, 3/4 inch liquid layer thickness, and pH 9 buffered with Trizma and HCl:

Dye	Dye Conc. (mg/1)	$-k(\text{min}^{-1})$
Methylene Blue	5	0.100
Hematoporphyrin-D,L-hydrochloride	5	0.045
Rose Bengal	5	0.092
Acridine Orange	5	(phenol = 42 mg/1 after 10 min)
2,7-Dichlorofluorescein	5	0.000
Malachite Green	5	(phenol = 42 mg/1 after 10 min)
Rhodamine 6G	5	(phenol = 43 mg/1 after 10 min)

With 50 mg/l initial cresol, 5 mg/l methylene blue, and 3/4 inch liquid layer thickness:

pH	Buffer Material	$-k(\text{min}^{-1})$
5.4	KH_2PO_4 and NaOH	0.016
6.1	KH_2PO_4 and NaOH	0.016
7.2	Trizma and HCl	0.044
7.8 to 7.2	unbuffered	0.082
8.3	Trizma	0.139
8.6	Trizma and HCl	0.114
8.7	Trizma and HCl	0.179
10.0	$NaHCO_3$ and HCl	0.333

With 50 mg/l initial cresol, 5 mg/l methylene blue, 3/4 inch liquid layer thickness, and buffered with $NaHCO_3$ and NaOH:

pH	$NaHCO_3$ Conc(moles/l)	NaOH Conc(moles/l)	$-k(\text{min}^{-1})$
8.8	5.95×10^{-3}	5×10^{-4}	0.269
9.0	1.19×10^{-2}	1×10^{-3}	0.246
9.3	3.57×10^{-2}	3×10^{-3}	0.262
9.2	5.95×10^{-2}	5×10^{-3}	0.220

With 50 mg/1 initial cresol, 3/4 inch liquid layer thickness, and pH 9 buffered with $NaHCO_3$ and NaOH:

Methylene Blue Concentration (mg/1)	$-k(min^{-1})$
1	0.161
3	0.238
5	0.250
7	0.246
10	0.204
15	0.169

With 5 mg/1 methylene blue, 3/4 inch liquid layer thickness, and pH 9 buffered with $NaHCO_3$ and NaOH:

Cresol Concentration (mg/1)	$-k(min^{-1})$
20	0.160
50	0.280
100	0.196
200	0.121
300	0.065

With 100 mg/l initial cresol, 5 mg/l methylene blue, and pH 9 buffered with $NaHCO_3$ and NaOH;

Liquid Layer Thickness (inches)	$-k(min^{-1})$
1/4	0.291
3/4	0.201
1 1/4	0.107
1 3/4	0.092

With 100 mg/l initial cresol, 5 mg/l methylene blue, 3/4 inch liquid layer thickness, and pH 9 buffered with $NaHCO_3$ and NaOH:

Light Intensity (% of full intensity)	$-k(min^{-1})$
100	0.201
85.6	0.116
79.2	0.121
53.9	0.094

With 100 mg/l initial cresol, 3/4 inch liquid layer thickness, and pH 9 buffered with $NaHCO_3$ and NaOH;

Resin (coated with methylene blue)	$-k(min^{-1})$
Dowex HCR	0.035
Duolite C-25D	0.051
Duolite ES-80	0.038
Duolite C-20X4	0.008
Powdex (PCH)	0.005

With 100 mg/l initial cresol, 3/4 inch liquid layer thickness, pH 9 buffered with $NaHCO_3$ and NaOH, and methylene blue bound to C-20X4 resin:

Milligrams Dye Bound to 100 ml Resin	$-k(min^{-1})$
4.0	0.013
30.0	0.004
70.0	0.008
99.8	0.014
999.7	0.009
4900	0.008
25000 (approx)	0.070 (dye coming off resin and into solution during test)

SAMPLE COMPUTER PRINTOUT

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ENTRY INTO ERROR

      Y-MEAS             Y-CALC             DEV              PERCENT
      50.000000          49.289398          .710602          1.421203
        .001000
      46.000000          43.974182         2.025818          4.403952
       1.000999
      36.000000          39.232117        -3.232117         -8.978098
       2.000999
      38.000000          35.001450         2.998550          7.890922
       3.000999
      29.000000          31.227005        -2.227005         -7.679325
       4.000999
      28.000000          27.859558          .140442           .501578
       5.000999
      16.000000          15.746933          .253067          1.581669
      10.000999

STANDARD DEVIATION EQUALS    2.202

AVERAGE PERCENT DEVIATION EQUALS      -.12259

 57.143 PERCENT OF DATA POINTS WITHIN 5.000 PERCENT OF THE EQUATION

100.000 PERCENT OF DATA POINTS WITHIN 10.000 PERCENT OF THE EQUATION

100.000 PERCENT OF DATA POINTS WITHIN 15.000 PERCENT OF THE EQUATION

100.000 PERCENT OF DATA POINTS WITHIN 20.000 PERCENT OF THE EQUATION

100.000 PERCENT OF DATA POINTS WITHIN 25.000 PERCENT OF THE EQUATION
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